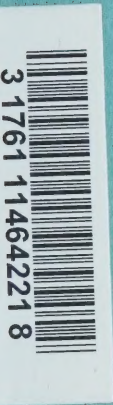


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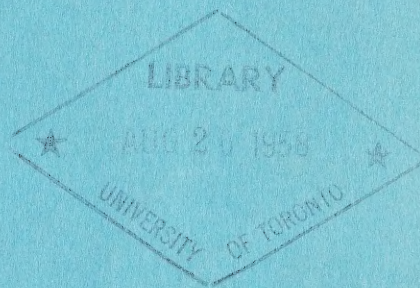


# **CHEMICAL METHODS OF SOIL ANALYSIS**

Assembled and Edited

by

H. J. ATKINSON, G. R. GILES,  
A. J. MacLEAN AND J. R. WRIGHT



CONTRIBUTION No. 169 (REVISED)  
CHEMISTRY DIVISION — SCIENCE SERVICE  
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## FOREWORD

This publication was first prepared in 1946, following the receipt of a large number of requests for information on chemical methods used in soil analysis. It was revised in 1949. Since that time, new methods of estimating the availability of soil phosphorus have been proposed, the use of ethylenediaminetetraacetic acid (EDTA) in analytical procedures has developed considerably, and the flame photometer has become almost a standard piece of laboratory equipment. Hence a further revision has become imperative at this time.

The needs of non-professional analysts have been kept in mind during preparation of this publication. Part I comprises a general discussion of the subject, describing the purpose for which each determination is made, the usual procedure followed and information that can be obtained. Part II contains details of methods of analysis used in the soils laboratories of the Chemistry Division. It is hoped that this publication will provide a ready reference for those interested in soil analysis.

The authors wish to acknowledge the assistance of the following members of the staff of the Soil Chemistry Unit in the preparation of these methods for publication: J. G. Desjardins, R. L. Halstead, R. Levick and S. I. M. Skinner.

H. J. Atkinson,  
Head, Soil Chemistry Unit.




## PREFACE TO THE SERIES

The application of chemistry to the solution of problems in animal, plant and soil science entails the development and standardization of methods applicable to the material under study. Chemical methods of soil analysis were compiled in 1946 and revised 1949. Chemical methods of plant analysis were assembled in 1953, and in 1956 chemical methods for analysis of fruit and vegetable products. Dr. Atkinson and his colleagues have now made a further revision of chemical methods of soil analysis.

These booklets are for the convenience of laboratory personnel: they do not take the place of standard works such as the A.O.A.C. Methods of Analysis.

A. R. G. Emslie, Chief,  
Chemistry Division,  
March, 1958





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PART I

GENERAL OBSERVATIONS

ON

CHEMICAL METHODS

OF

SOIL ANALYSIS





## INTRODUCTION

Soil samples are submitted for analysis and examination for a variety of reasons. In general, they can be classified into three groups:

1. Those taken to obtain information on the basis of which soils can be classified into groups and the characteristic properties of each group established. Soil surveyors are most frequently interested in this type of information.
2. Those taken to determine changes taking place in soils as the result of various treatments such as methods of cultivation, crop rotations, and applications of manures, fertilizers and amendments. Agronomists and soil fertility specialists desire information of this kind.
3. Those taken to establish fertility levels and to indicate treatments required to increase crop yields. Farmers and gardeners frequently seek advice on management practices based on the testing of soil samples. Soil testing for individuals is fairly well organized under Provincial Departments of Agriculture at the present time and this service is no longer available in the Chemistry Division at Ottawa.

The various determinations most commonly made in soil analysis will be discussed in general terms in the following pages, with details of methods being given in Part II. For those interested in reading other publications on the subject of soil analysis, or of chemical methods that may be used for soils, the following references may prove useful:

1. Association of Official Agricultural Chemists. Official and tentative methods of analysis. 8 Ed. 1955. Published by the A.O.A.C., P.O. Box 540, Benjamin Franklin Station, Washington 4, D.C., U.S.A.
2. Hillebrand, W.F., G.E.F. Lundell, H.A. Bright and J.I. Hoffman. Applied inorganic analysis. John Wiley & Sons, New York. 1953.
3. Metson, A.J. Methods of chemical analysis for soil survey samples. N.Z. Dept. Sci. Ind. Research, Soil Bureau Bul. 12. 1956.
4. Peech, M., L.T. Alexander, L.A. Dean and J.F. Reed. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agr. Circ. 757. 1947.
5. Piper, C.S. Soil and plant analysis. Interscience Publishers, Inc., New York, N.Y. 1944.
6. Prince, A.L. Methods in soil analysis. In Chemistry of the soil. Am. Chem. Soc. Monograph Ser. No. 126. Reinhold Publishing Corp., New York. 1955.
7. Soil Science. Methods in chemical analysis of soil. In the January issue of Vol. 59. 1945. Published by the Williams & Wilkins Co., Baltimore 2, Md., U.S.A.

## PREPARATION OF SAMPLE FOR ANALYSIS

Before analysis soil samples should be spread out in thin layers and allowed to dry at room temperature. The portion of air-dry material that can be passed through a screen with openings 2 mm. in diameter is used for analysis. When it is desirable to know the amount of the sample that does not pass the 2 mm. screen, it is weighed and expressed as a percentage of the original soil.

For determination of soil reaction, readily soluble phosphorus and exchangeable bases, the 2 mm. material is used. For determination of hygroscopic moisture, loss on ignition and total nitrogen, some of the 2mm. sample is ground to pass a screen with openings 1/2 mm. in diameter. When the total quantity of any constituent other than nitrogen is to be determined, some of the 1/2 mm. material is ground to pass a screen containing 100 meshes to the inch.

When trace elements are to be determined, extreme care is necessary to avoid contamination from outside sources. Metal screens must be avoided. Screening should be done through non-metallic material and grinding should take place in an agate mortar.

### SOIL REACTION (pH)

The reaction of a soil is a very important characteristic and its determination is, in most cases, the first to be made in the laboratory. It shows whether a soil is acid, neutral or alkaline, as well as the degree of acidity or alkalinity.

Soil reaction is commonly expressed by a series of values from 0 to 14, known as pH values. For most soils, these figures lie between 4.5 and 9.0 and the degrees of acidity are indicated approximately as follows:

Very strongly acid	pH 3.5 to 4.4
Strongly acid	pH 4.5 to 5.4
Moderately acid	pH 5.5 to 6.1
Slightly acid	pH 6.2 to 6.7
Neutral	pH 6.8 to 7.2
Mildly alkaline	pH 7.3 to 8.0
Moderately alkaline	pH 8.1 to 9.0
Strongly alkaline	pH 9.1 and over

Although neutrality is precisely pH 7.0, for practical purposes soil samples having pH values of 6.8 to 7.2 may be considered neutral.

Reaction is frequently determined by means of indicator solutions, i.e. solutions of organic substances which change in color with different degrees of acidity or alkalinity. A small quantity of soil is mixed with some indicator solution and the resulting color compared with a chart having colors which correspond with definite pH values. Different indicators are used for different ranges of pH. Indicator sets can be obtained for rapid pH determinations in the field.



More reliable determinations of pH values are made in the laboratory by electrometric methods. Formerly, use was made of the quinhydrone and the hydrogen electrodes but most modern instruments use the glass electrode. Soil and water are mixed either in definite ratios (e. g. 1:1) or so as to form a paste, the electrode assembly is introduced and the measurements are taken on a potentiometer.

The activity of microorganisms, the availability of nutrients to plants, the solubility of soil constituents and their vertical movement in soil development processes are all affected by the reaction of the soil. Hence the importance of a knowledge of soil reaction is obvious. The estimation of the quantity of limestone required to neutralize soil acidity for plant growth is a very practical use of this information.

### HYGROSCOPIC MOISTURE

By hygroscopic moisture is meant moisture which is firmly held by absorption by colloidal material in the soil even after the soil had been allowed to dry completely in air. It is determined by drying a weighed amount of soil in an oven overnight at a temperature of about 105°C. This determination is carried out in order that results of analysis for different constituents can be calculated to a moisture-free basis and thus permit comparisons of data for different soil samples.

### LOSS ON IGNITION

Loss in weight resulting from igniting a soil in contact with air includes that due to combined water in the soil colloids, to combustion of organic matter and to decomposition of carbonates. The temperature recommended for determining loss on ignition varies and will depend on the information desired. When the ignition is carried out at a temperature of 420°C. to 450°C., the loss approximates the amount of organic matter in the sample, although the result so obtained is usually somewhat higher than that determined by calculation from the amount of carbon present. When the temperature of ignition is about 850°C., loss includes that due to decomposition of carbonates and to water which makes up part of the crystal structure of clay minerals. This higher temperature is used when total analysis of a sample is made.

### NITROGEN

While plants take up nitrogen in the inorganic form mainly as nitrates, practically all of the nitrogen is present in organic combinations. This is slowly released through the action of microorganisms and converted finally into nitrate and, as such, is readily assimilated by plants. The determination of organic nitrogen not only gives a measure of the total reserve supply of this element in the soil, but also gives an indication of the amount of organic matter, since the nitrogen is present roughly in proportion to the quantity of soil organic matter.

This determination is made on practically all soil samples received. A suitable quantity of each is digested in strong acid with appropriate catalyst, thus converting nitrogen to the ammonia form which can be distilled off and measured by chemical means.

The majority of Canadian soils contain between 0.10 and 0.30 per cent of nitrogen, though a considerable number reach 0.50 per cent. Peats and mucks usually contain from 1.0 to 2.0 per cent. Soils containing less than 0.15 per cent may prove fairly productive under conditions favorable for nitrification but in general they respond profitably to nitrogenous fertilizers.

In addition to organic combinations, nitrogen exists in the soil also in the ammonium, nitrite and nitrate forms, but these are present in very small quantities usually measurable only in parts per million of soil. Nitrates constitute most of the direct source of plant nitrogen but the quantities present in a soil sample are profoundly influenced by such factors as proximity to the plant, rainfall, temperature and microbiological activity. Consequently the information obtained from a determination of nitrates is limited and must be interpreted in the light of the other factors mentioned. Determinations of other forms of nitrogen are usually made only when specific problems are under study.

## ORGANIC MATTER AND CARBON

Organic matter helps to improve the soil's physical condition, promotes the growth of micro-organisms and is a storehouse for plant food. It has already been pointed out that an approximate idea of the amount of organic matter present can be obtained from the loss on ignition and from the nitrogen content. There are also a number of methods available for the direct determination of organic matter. However, it is considered by many that the most reliable method of estimating soil organic matter is to determine the amount of organic carbon present and multiply the result by 1.724. This factor is based on the assumption that soil organic matter contains 58 per cent of carbon.

There are two general ways of determining the organic carbon of soils. One is by treatment of the soil sample with potassium dichromate and sulphuric acid to oxidize the organic matter. The carbon dioxide evolved can be absorbed and weighed, or the amount of potassium dichromate that has been reduced can be determined by titration. In the other general method, the soil is heated in a stream of oxygen until the organic matter is completely oxidized, and the amount of carbon dioxide evolved is carefully collected and determined. This is known as the dry combustion method and is usually regarded as standard. In soils that contain carbonates such as calcium carbonate, the amount of carbon in this inorganic form has to be either removed before the organic carbon determination or determined separately and subtracted from the total.

Soils well supplied with organic matter usually have a higher level of fertility than those poorly supplied, because this constituent contributes to the water-holding capacity, the base exchange capacity and the gradual release of plant nutrients. Hence a measure of the organic matter content of soil samples is very desirable.



### PHOSPHORUS (total)

Soil phosphorus is found partly in organic combinations and partly in complex mineral forms. In determining the total quantity present, it is necessary first to oxidize the organic matter to convert its phosphorus to the inorganic form and then to bring all the phosphorus into solution. This can be done by one of several wet digestion methods or by fusion. When in solution, phosphorus can be readily determined.

This element is one of the three plant nutrients most frequently applied in fertilizers. It is of some interest to know the total amount present in a soil. The total phosphorus in Canadian soils of average fertility usually lies between 0.06 and 0.11 per cent P. Some very good loams contain 0.11 to 0.13 per cent P and a few exceed the latter figure.

### PHOSPHORUS (available)

Only a small fraction of the total phosphorus of a soil is available to plants at any time. From the point of view of soil fertility and for the purpose of making fertilizer recommendations, it would be very useful to know how much is available. This is something that cannot be determined absolutely. However, attempts have been made to estimate the size of this fraction by extracting the soil with various chemical solutions and finding out how much phosphorus is thus dissolved. Some chemists prefer one solution, some another. The amount of phosphorus thus extracted, however, does not measure any definite chemical fraction but it has been found, within limits, that if the quantity of phosphorus extracted by one of these reagents is below a certain value, it is probable that the soil will respond to applications of a phosphatic fertilizer. Such methods are not universally applicable, however, and should be calibrated against the response of different crops to fertilizers on different soil types before definite predictions as to fertilizer needs can be made from such determinations.

In addition there are a number of biological methods of determining the amount of available phosphorus in a soil sample. In these, growing plants as in the Neubauer method, or micro-organisms are used to measure the extent to which the element is readily available as a plant nutrient.

### EXCHANGEABLE CATIONS (Ca, Mg, K, Na, H)

A very important part of the soil is that which is made up of those very fine particles, probably less than 0.002 mm. in diameter, whose surface areas are very large in comparison with their mass and which are thus very active chemically. These particles form what is known as the colloidal complex, made up of decomposed organic matter and crystalline clay minerals. It has been found that the soil colloidal complex holds on its surface, by adsorption, a number of ions, of which those of calcium, magnesium, potassium and sodium are most important. In acid soils, hydrogen ions are found in greater or lesser amount according to the degree of acidity. These ions are readily replaced by chemical action and are known as exchangeable or replaceable cations. They are very important from the point of view of soil fertility



and plant nutrition, since they constitute the most readily accessible source of these elements for the plant roots.

The determination of the exchangeable cations is usually made by extracting the soil with a solution of a neutral salt. While a number of salts have been used for this purpose by various workers, the one most commonly used is ammonium acetate as a normal solution adjusted to pH 7.0. The best procedure appears to be one of leaching whereby the replaced cations pass into the filtrate and the soil continues to be leached with fresh portions of the acetate solution. The exchangeable cations are thus completely replaced by the ammonium ion, and are determined in the filtrate or leachate by standard methods.

The sum of the bases mentioned, (calcium, magnesium, potassium and sodium) together with the exchangeable hydrogen if any is present, gives approximately the base exchange capacity of the soil. Sometimes it is desirable to know this capacity without the necessity of determining the individual ions. This can be done by removing the excess ammonium acetate solution from the soil sample, e. g. by leaching with neutral alcohol, and determining the amount of ammonia that has been adsorbed by the soil.

The amounts of exchangeable bases are usually taken as indications of the quantities of these elements that are available to plants. In most routine work, it is customary to determine only the amounts of calcium, magnesium and potassium. The amount of calcium present, when considered in conjunction with the soil reaction, will indicate whether or not lime should be added. In a calcareous soil, the amount of calcium found in the ammonium acetate leachate usually is greater than that actually present in the exchangeable form because some of the calcium carbonate has been brought into solution. Magnesium is usually present in sufficient quantities, though, in some districts, certain crops, particularly apples, potatoes and tobacco, have shown symptoms of magnesium deficiency. The amount of exchangeable potassium is important, since this element is one of the three most common plant nutrient constituents of commercial fertilizers. Experience has shown that, in a great many cases, when the amount of exchangeable potassium is below a certain value, crop response to added potassic fertilizers may be expected. To establish this minimum value, it is necessary to compare the results of chemical analysis with response to applied potassium in the field, and such comparisons may be expected to vary with soil type, crop and climatic conditions.

#### MAJOR CONSTITUENTS (other than N, C and P)

(Si, Fe, Al, Ti, Ca, Mg, K, Na)

The analysis of soil samples for the determination of total quantities of silicon, iron, aluminum, titanium, calcium, magnesium, potassium and sodium, is usually carried out only on samples submitted by soil surveyors, where information is desired in the classification of soils. All constituents except silica can be brought into solution following the fusing of the soil with anhydrous sodium carbonate. The silica can be measured after dehydration and the other elements can be determined in solution by standard procedures. For the determination of

sodium and potassium, it is customary to make a separate fusion, using calcium carbonate and a small amount of ammonium chloride. In cases where the determination of silica is not considered necessary or where it is desirable to avoid an alkaline solution of the other constituents, the silica can be removed by treating the soil sample with hydrofluoric acid and the other constituents brought into solution.

A knowledge of the total amounts of these constituents in the horizons of a soil profile gives a measure of the degree of weathering and leaching that has taken place in soil formation and aids materially in the proper classification of the soil.

### MINOR CONSTITUENTS

(B, Mn, Cu, Co, Zn, Mo)

There is a group of elements of great importance in soil fertility studies which are known collectively as the trace elements or, alternatively, minor elements or micro-nutrients. They are required by plants in only very small amounts but their absence causes pronounced physiological disorders. On the other hand, if they are present in excess they have a toxic effect and the range between insufficiency and excess is relatively narrow. This group includes boron, manganese, copper, zinc and molybdenum. Cobalt is usually classed as a trace element because, although plants are not known to suffer from lack of it, animals develop a disorder when fed on plants low in this element. Boron soluble in hot water and manganese present in exchangeable and easily-reducible forms are considered to be readily available to plants. There is as yet no really satisfactory chemical method for estimating the availability of the other trace elements, though microbiological methods are used successfully in some laboratories.

There are other elements found in soils in very small quantities for which methods of analysis have been developed. Among these may be mentioned selenium, arsenic, iodine, fluorine, chlorine, vanadium and lead. Determinations of these are usually made only when special problems are under investigation.





PART II

DETAILS OF THE METHODS

USED IN THE

SOIL CHEMISTRY LABORATORIES

OF THE

CHEMISTRY DIVISION



## PREPARATION OF SAMPLE

If sample as received is moist, spread on a sheet of clean paper to air-dry. When dry, mix thoroughly. Remove approx. 1/2 pint for sieving and store remainder in cardboard carton.

Pass the 1/2 pint of air-dry sample removed above through a 2 mm. screen (except for trace element determination - see below). Remove roots leaves and other coarse vegetable material. Crush lumps by rubbing in a porcelain mortar or by other equally effective method that will not crush rock fragments.

Weigh both material that has passed through screen and that retained by screen. Calculate each as per cent of weight of total sample. Discard material retained by 2 mm. screen.

Thoroughly mix material that has passed 2 mm. screen by rolling it on a sheet of paper. Remove approx. 100 g. for grinding and store remainder in a cardboard container. Use 2 mm. material for determining pH, easily soluble P and exchangeable cations.

Grind the 100 g. sample removed above until all particles pass through a 1/2 mm. screen. Use 1/2 mm. material for determining hygroscopic moisture, loss on ignition and total nitrogen.

If total quantity of any constituent (other than nitrogen) is to be determined, remove an additional 50 g. sample from 2 mm. material and grind until all has passed a 100-mesh screen.



For trace element analysis, pass approx. 50 g. air-dry sample through cheesecloth with openings approx. 2 mm. Mix thoroughly and grind approx. 10 g. in agate mortar until it appears to be fine enough to pass 200-mesh but do not sieve. Use this for totals. Retain remainder of 2 mm. material for ex. Mn and water-sol. B determinations .

pH VALUE

Procedure

Weigh 10 g. of 2 mm. material into a 50 ml. beaker or waxed paper cup. Add 10 ml. water and stir. Stir again after 5 min. and after 10 min. and remove stirring rod. At end of 15 min. from time water is added, introduce glass electrode and take reading after 1 min. Check reading at half-minute intervals until constant reading is obtained. This usually does not take more than 3 or 4 min.

## HYGROSCOPIC MOISTURE

### Procedure

Weigh 2 g. of 1/2 mm. material into a previously ignited porcelain crucible. Dry in oven overnight at 105 °C. Weigh . Calculate loss in weight as per cent of moisture-free soil .

(With samples which are to be analyzed for total constituents, determine hygroscopic moisture and loss on ignition on 100-mesh material.)



## LOSS ON IGNITION

### Procedure

This determination is made on sample used for hygroscopic moisture determination.

(a) In case of a sample which is being analyzed for total constituents heat crucible containing dry soil in muffle furnace to  $850^{\circ}\text{C}$ . and maintain there for  $1/2$  hour. (This should decompose carbonates as well as drive off organic matter and combined water in soil colloids). Cool and weigh. Calculate loss in weight as per cent of moisture-free soil.

(b) In case of a sample for fertility studies, place crucible containing dry soil in muffle furnace at room temperature and heat slowly to  $420^{\circ}\text{C}$ . Maintain at  $420^{\circ}$  to  $450^{\circ}\text{C}$ . for 45 min. in case of mineral soils and 1 to  $1-1/2$  hr. in case of organic soils. Cool and weigh. Calculate loss in weight as per cent of moisture-free soil.

## ORGANIC MATTER

### Reagents

1. Potassium dichromate solution - 1.0 N. Dissolve 49.04 g. reagent grade  $K_2Cr_2O_7$  in water and dilute to 1 liter. Mix thoroughly.
2. Ferrous sulphate solution - 0.5 N. Dissolve 140 g. reagent grade  $FeSO_4 \cdot 7H_2O$  in water, add 40 ml. conc.  $H_2SO_4$ , cool and dilute to 1 liter. Mix thoroughly. Standardize daily by titrating against 10 ml. N  $K_2Cr_2O_7$  solution as directed in method below.
3. Barium diphenylaminesulphonate indicator solution. Prepare 0.16% aqueous solution.
4. Sulphuric acid -  $H_2SO_4$ , conc., not less than 96%.
5. Phosphoric acid -  $H_3PO_4$ , 85%, U. S. P. grade.

### Procedure

Weigh 0.5 g. of 1/2 mm. material, place in a 1000 ml. beaker and add 10 ml. N  $K_2Cr_2O_7$  solution. Then add rapidly 20 ml. conc.  $H_2SO_4$ , directing stream into solution. Immediately swirl vigorously by hand for 1 min and let beaker stand on a sheet of asbestos for 30 min.

Add 500 ml. water, 10 ml.  $H_3PO_4$  and 1.0 ml. of indicator solution. Use a motor-driven stirrer. From a burette, add  $FeSO_4$  solution rapidly until liquid in beaker is purple or blue, then more slowly until color flashes to green. If end point is passed, add a small volume (0.5 ml.) of N  $K_2Cr_2O_7$  solution and complete titration. If more than 8 of the available 10 ml. of  $K_2Cr_2O_7$  solution is reduced, repeat determination with less soil

$$\% \text{ organic matter in soil sample} = \frac{(\text{ml. N } K_2Cr_2O_7 \text{ reduced}) \times 0.69}{\text{weight of sample (g)}}$$

Reference

- (1) Peech, M., L. T. Alexander, L. A. Dean and J. F. Reed.  
Methods of soil analysis for soil-fertility investigations.  
U.S. Dept. Agr. Circ. 757. 1947.

## NITROGEN, TOTAL

### Reagents

1. Sulphuric acid -  $\text{H}_2\text{SO}_4$ , conc.
2. Potassium sulphate -  $\text{K}_2\text{SO}_4$ .
3. Copper sulphate -  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .
4. Sodium hydroxide -  $\text{NaOH}$ , 30% solution.
5. Boric acid -  $\text{H}_3\text{BO}_3$ , 4% solution.
6. Sulphuric acid - standard 0.1 N  $\text{H}_2\text{SO}_4$ .
7. Bromphenol blue indicator - Boil 0.1 g. in 3 ml. 0.05 N  $\text{NaOH}$  and dilute to 250 ml. with water.

### Procedure

Weigh duplicate 5 g. samples (2 g. in case of organic soils) of 1/2 mm. material and place in kjeldahl flasks. To each add 30 to 40 ml. conc.  $\text{H}_2\text{SO}_4$ , 10 g.  $\text{K}_2\text{SO}_4$  and 0.8 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Digest for 3 hr. Cool. Transfer with water to a copper flask. Add a piece of metallic Zn. Make alkaline with 80 ml. 30%  $\text{NaOH}$  solution and shake. Distill 150 ml. into approx. 50 ml. of 4% boric acid solution. Titrate direct with standard  $\text{H}_2\text{SO}_4$ , using bromphenol blue indicator (0.7 ml.)

$$1 \text{ ml. } 0.1 \text{ N } \text{H}_2\text{SO}_4 = 1.4 \text{ mg. N}$$



## CARBON, INORGANIC

### Reagents

1. Potassium hydroxide - KOH, 30% solution .
2. Soda lime .
3. Silver sulphate - pumice mixture - Mix 5 g.  $\text{Ag}_2\text{SO}_4$  and 20 g. pumice .  
Moisten with 5 ml. conc.  $\text{H}_2\text{SO}_4$  and mix thoroughly .
4. Hydrochloric acid - HCl, dilute (1+3) .
5. Barium hydroxide - standard 0.1 N  $\text{Ba}(\text{OH})_2$  .
6. Hydrochloric acid - standard 0.1 N HCl .
7. Phenolphthalein indicator - Dissolve 1 g. in 100 ml. 95%  $\text{C}_2\text{H}_5\text{OH}$  .

### Equipment

1. A purification train for removing  $\text{CO}_2$  from the air, consisting of (a) a gas washing bottle containing 30% KOH and (b) a tower of soda lime .
2. A generating flask, consisting of a wide-mouth bottle or flask of about 125 ml. capacity, fitted with a 2-hole rubber stopper holding a separatory funnel (which reaches nearly to the bottom of the bottle) and a small vertical condenser (the end of which just passes through the rubber stopper) .
3. A U-tube containing silver sulphate - pumice mixture, to absorb any HCl which might pass the condenser .
4. An absorption train consisting of (a) a meyer 10-bulb absorption tube containing standard 0.1 N  $\text{Ba}(\text{OH})_2$  solution, and (b) a 750 ml. erlenmeyer flask also containing a little of the standard  $\text{Ba}(\text{OH})_2$  solution (to absorb the  $\text{CO}_2$  evolved)
5. A suction pump to draw a current of gas through the apparatus .

### Equipment (Cont'd)

6. Rubber and glass tubing, rubber stoppers, etc., as required to connect the above pieces of apparatus into one complete assembly in the order listed above.

### Procedure

Depending on amount of carbonates present, weigh 0.50 to 5.00 g. 100-mesh soil and place in generating flask. Put 50 ml. HCl (1+3) in separatory funnel. Measure 50 ml. standard 0.1 N  $\text{Ba(OH)}_2$  solution, putting 2 to 3 ml. in erlenmeyer flask next to suction pump, and remainder in meyer absorption tube. Dilute standard  $\text{Ba(OH)}_2$  solution with water so that bulbs of absorption tube will be filled when gas is passing through it, and level of liquid in erlenmeyer flask will be above bottom of tube which is connected to end of absorption tube. (This is merely a safeguard in case some  $\text{CO}_2$  is not absorbed in the meyer tube). Connect apparatus together.

Run acid from separatory funnel slowly into soil and draw a slow current of  $\text{CO}_2$ -free air through apparatus for 1-1/2 to 2 hr. Pour contents of meyer absorption tube into 750 ml. erlenmeyer flask and wash tube two or three times with water into same flask. Titrate excess  $\text{Ba(OH)}_2$  with standard 0.1 N HCl solution, using phenolphthalein as indicator. Calculate amount of carbon in soil sample from amount of  $\text{Ba(OH)}_2$  that was converted to  $\text{BaCO}_3$ , and express as C,  $\text{CO}_2$  or  $\text{CaCO}_3$  as desired. A blank determination should be made.

### Reference

Mahin, E. G. and R. H. Carr. Quantitative agricultural analysis (pp. 77-85, 249). 1st Ed. McGraw-Hill Book Co. Inc., New York. 1923.

## PHOSPHORUS, TOTAL

### Reagents

1. Sodium carbonate -  $\text{Na}_2\text{CO}_3$ , anhydrous .
2. Dinitrophenol indicator - Dissolve 0.1 g. 2,6-dinitrophenol in 100 ml. aqueous ethyl alcohol containing 25 ml.  $\text{C}_2\text{H}_5\text{OH}$  .
3. Sulphuric acid - Add 100 ml. conc.  $\text{H}_2\text{SO}_4$  to 900 ml. water .
4. Tartaric acid solution - Dissolve 20 g. tartaric acid  $(\text{CHOH})_2(\text{COOH})_2$  in 1 liter of water .
5. Sodium molybdate solution - Dissolve 20 g.  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 1 liter of aqueous  $\text{H}_2\text{SO}_4$  containing 160 ml. conc.  $\text{H}_2\text{SO}_4$  .
6. Hydrazine sulphate solution - Dissolve 20 g. hydrazine sulphate  $(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4)$  in 1 liter of water .
7. Standard phosphorus solution - Dissolve 0.8785 g. dry  $\text{KH}_2\text{PO}_4$  in water and dilute to 1 liter. Mix thoroughly. Dilute 100 ml. of this solution to 1 liter with water. 1 ml. = 0.02 mg. P.

### Procedure

Weigh 0.5 g. 100-mesh soil into Pt crucible. Add 2 to 4 g. anhydrous  $\text{Na}_2\text{CO}_3$  and mix thoroughly. Cover mixture with thin layer of  $\text{Na}_2\text{CO}_3$ . Heat crucible gently with meker burner to drive off moisture. Place lid on crucible and regulate flame so that mass fuses gently. Continue heating at full blast of meker burner for 10 min .

Remove flame. Take off lid and rotate crucible as it cools so as to distribute fused mass as thin layer over interior. When crucible is cool enough to touch, roll it gently between hands to facilitate removal of melt, then place in a 250 ml. beaker containing 150 ml. hot water. Set beaker on a water bath at  $100^\circ\text{C}$ . for 2 hr .



### Procedure (Cont'd)

Remove melt from crucible, rubbing gently with a glass rod if necessary. Rinse crucible and lid into beaker, which is placed on water-bath for a further 30 min. After cooling, dilute suspension to 250 ml. with water and mix well. Filter two or three times with suction through same Whatman No. 42 filter paper to ensure clear filtrate.

Transfer aliquot (not exceeding 50 ml.) of filtrate into 300-ml. erlenmeyer flask and dilute to 150 ml. with water. Add two drops of indicator and just discharge color by adding sulphuric acid reagent from burette. Add 10 ml. tartaric acid reagent, followed by 5 ml. sodium molybdate and 5 ml. hydrazine sulphate reagents. Heat to boiling and boil for 1 min. after blue color appears. (If color does not appear within 1 min. of boiling, cool solution and add further 5 ml. hydrazine sulphate reagent (amount is not critical), and boil solution again for 1 min.) Let cool and dilute to 200 ml. in volumetric flask. Mix thoroughly and determine color intensity with photoelectric colorimeter using red filter. Color is stable for 24 hr.

Calculate amount of P from curve prepared as follows: Measure suitable aliquots (1 to 15 ml.) of standard phosphate solution (1 ml. = 0.02 mg. P) into 300 ml. erlenmeyer flasks, dilute to 150 ml. with water and proceed as in previous paragraph from where it says: "Add two drops of indicator . . . . .". Express as % P in dry soil.

### Reference

1. Muir, J.W. The determination of total phosphorus in soil, Analyst 77: 313-317. 1952.

## PHOSPHORUS, EASILY-SOLUBLE

(Bray method - Acid-soluble plus adsorbed P)

### Reagents

1. Extracting solution (P-A) - Add 30 ml. 1.0 N  $\text{NH}_4\text{F}$  and 200 ml. 0.5 N HCl to 770 ml. water. Store in polyethylene bottle. (This solution is 0.03 N in  $\text{NH}_4\text{F}$  and 0.1 N in HCl).
2. Molybdate reagent - Add, with stirring, a solution of 10 g. ammonium molybdate ( $(\text{NH}_4)_2\text{MoO}_4$ ) in 85 ml. water to cold solution consisting of 16 ml. water in 170 ml. conc. HCl.
3. Amino-naphthol-sulphonic acid reagent - Mix thoroughly 2.5 g. 1-amino-2-naphthol-4-sulphonic acid, 5.0 g. sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) and 146.25 g. sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ), and grind mixture to fine powder. Dissolve 8.0 g. of mixture in 50 ml. warm water and allow to stand overnight before use. Prepare fresh solution every 3 weeks.
4. Standard phosphorus solution - Dissolve 0.2194 g. dry  $\text{KH}_2\text{PO}_4$  in water and dilute to 1 liter. Mix thoroughly. This solution contains 50 p.p.m. P.

### Procedure

Place 1 g. soil in 50-ml. erlenmeyer flask, add 10 ml. extracting solution (P-A), shake for 40 sec. and filter through Whatman No. 42 filter paper.

Transfer 5 ml. filtrate into colorimeter tube. Add 0.2 ml. molybdate reagent and mix. Add 0.2 ml. amino-naphthol-sulphonic acid reagent, mix and let stand for 15 min. Determine color intensity with photoelectric colorimeter using a red filter.

Calculate amount of P from curve prepared as follows: Dilute suitable

### Procedure (Cont'd)

aliquots of standard phosphate solution to 50 ml. with water to give concentrations of 0 to 10 p.p.m. P. Transfer 5 ml. of each to colorimeter tubes and proceed as in previous paragraph from where it says: "Add 0.2 ml. molybdate reagent . . . . ." Express as p.p.m. air-dried soil.

### References

1. Bray, R.H. Correlation of soil tests with crop response to added fertilizer and with fertilizer requirement. Diagnostic techniques for soils and crops, pp. 53-86. The American Potash Institute, Washington, D.C. 1948.



## PHOSPHORUS, EASILY-SOLUBLE

(Olsen's  $\text{NaHCO}_3$  method)

### Reagents

1. Extracting solution ( $0.5 \text{ M NaHCO}_3$ ) - Dissolve 42.01 g  $\text{NaHCO}_3$  in water and dilute to 1 liter. Mix thoroughly.  
Adjust reaction to pH 8.5 with  $\text{NaOH}$
2. Carbon black (Darco - G - 60) - Pre-treat by leaching with  $\text{NaHCO}_3$ -extracting solution, washing with water and drying.
3. Ammonium molybdate - hydrochloric acid solution - Dissolve 15g. C. P.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in about 300 ml. warm ( $50^\circ\text{C}.$ ) water. Filter if necessary. When solution has cooled, add 400 ml.  $10.0 \text{ N HCl}$  slowly with shaking to molybdate solution. Cool to room temperature and dilute to 1 liter with water. Mix thoroughly. Store in black, glass-stoppered bottle. Replace with fresh solution every 2 months.
4. Stannous chloride
  - a. Stock solution. Dissolve 10 g.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 25 ml. conc  $\text{HCl}$ . Store in black glass-stoppered bottle. Replace with fresh solution every 2 months.
  - b. Dilute solution. Add 1.0 ml. stock solution to 265 ml. water and mix. Prepare fresh solution every 8 hr.
5. Standard phosphorus solution - Dissolve 0.2194 g. dry  $\text{KH}_2\text{PO}_4$  in water and dilute to 1 liter. Mix thoroughly. This solution contains 50 p.p.m. P. Dilute 10 ml. of this solution to 500 ml. with water to provide solution containing 1 p.p.m. P. Mix thoroughly.

## Procedure

Place 5 g. soil and 1 teaspoonful carbon black in 200 ml. erlenmeyer flask. Add 100 ml. extracting solution and shake for 30 min. Filter through Whatman #42 filter paper.

Transfer 5 ml. of filtrate into 50 ml. graduated cylinder provided with ground glass stopper. Dilute with water to approx. 15 ml. Add 5 ml. molybdate solution and mix gently to avoid loss of solution due to rapid evolution of  $\text{CO}_2$ . When evolution of  $\text{CO}_2$  has subsided, wash down sides of cylinder with water and dilute to exactly 23 ml. Add 2 ml. dilute  $\text{SnCl}_2$  solution with pipette and shake immediately. Let stand 15 min. Determine color intensity with photo-electric colorimeter, using a red filter.

Calculate amount of P from curve prepared as follows: Measure suitable aliquots (1 to 10 ml.) of standard phosphate solution (1 p.p.m. P) into graduated cylinders provided with ground glass stoppers. Dilute to 10 ml. with water and add 5 ml. extracting solution. Proceed as in preceding paragraph from where it says: "Add 5 ml. molybdate solution . . . ." Express as p.p.m. air-dried soil.

## References

1. Dickman, S.R. and R.H. Bray. Colorimetric determination of phosphate. Ind. Eng. Chem., Anal. Ed. 12: 665-668. 1940.
2. Olsen, S.R., C.V. Cole, F.S. Watanabe and L.A. Dean. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dept. Agr. Circ. 939. 1940.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 1. Extraction

#### Reagents

1. Ammonium acetate - 1.0 N solution. Dissolve 1540 g. ammonium acetate ( $\text{NH}_4\text{OAc}$ ) in water. Filter, dilute to 20 l. and mix thoroughly. Adjust to pH 7.0 with  $\text{NH}_4\text{OH}$  or  $\text{HOAc}$  as required.

#### Procedure

Place 25 g. soil in a 150 ml. beaker. Add 50 ml.  $\text{NH}_4\text{OAc}$  solution, stir and let stand overnight. Filter, with suction, through a buchner funnel fitted with 9.0 cm. Whatman #42 filter paper. Leach with small portions of  $\text{NH}_4\text{OAc}$  solution to a volume of less than 250 ml. Transfer solution from suction flask to a 250 ml. volumetric flask. Rinse suction flask with small amounts of  $\text{NH}_4\text{OAc}$  solution, adding them to contents of volumetric. Dilute to volume and mix thoroughly.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 2. Cation exchange capacity

#### Reagents

1. Ethyl alcohol -  $\text{C}_2\text{H}_5\text{OH}$ , 95%. 50 ml. of the alcohol plus 35 ml.  $\text{CO}_2$ -free water should not require more than 0.2 ml. 0.05 N NaOH to give a slight pink color with phenolphthalein.
2. Sodium chloride - NaCl, 10% solution, acidified. Prepare aqueous 10% solution, using ammonia-free salt, and acidify with HCl to render solution approx. 0.005 N with respect to acidity.
3. Antifoam mixture - Mix equal parts of mineral oil and capryl alcohol.
4. Sodium hydroxide - 1.0 N NaOH and standard 0.1 N NaOH.
5. Sulphuric acid - Standard 0.2 N  $\text{H}_2\text{SO}_4$ .
6. Methyl red indicator - Dissolve 0.5 g. in 100 ml. 95%  $\text{C}_2\text{H}_5\text{OH}$ .

#### Procedure

Leach excess  $\text{NH}_4\text{OAc}$  from  $\text{NH}_4$ -saturated soil in buchner funnel with 200 ml. 95%  $\text{C}_2\text{H}_5\text{OH}$ , using small portions and draining well between each addition. Determine adsorbed  $\text{NH}_3$  by either "a" or "b" below.

#### a. Extraction of adsorbed $\text{NH}_3$ prior to distillation

Leach alcohol-washed soil with 400 ml. NaCl solution, using small portions and draining well between each addition. Transfer filtrate to kjeldahl flask and add 25 ml. 1 N NaOH. Distill 200 ml. into 30 ml. standard 0.2 N  $\text{H}_2\text{SO}_4$  and titrate excess acid with standard 0.1 N NaOH, using methyl red indicator. (Or distill into boric acid and titrate, as described under "NITROGEN, TOTAL"). Express results as milliequivalents per 100 g. soil.

#### b. Direct distillation of adsorbed $\text{NH}_3$

Transfer alcohol-washed soil and filter paper to kjeldahl flask. Add 300



b. Direct distillation of adsorbed  $\text{NH}_3$  (Cont'd)

ml. water, 10 g.  $\text{NaCl}$ , 2.5 ml. antifoam mixture and 25 ml. 1 N  $\text{NaOH}$ .

Distill 200 ml. into 30 ml. standard 0.2 N  $\text{H}_2\text{SO}_4$  and titrate excess acid

with standard 0.1 N  $\text{NaOH}$ , using methyl red indicator. (Or distill into

boric acid and titrate, as described under "NITROGEN, TOTAL".) Express

results as milliequivalents per 100 g. soil.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 3. Treatment of extract

#### Reagents

1. Nitric acid -  $\text{HNO}_3$ , conc. and 0.1 N.
2. Hydrochloric acid -  $\text{HCl}$ , conc. and dilute (1+1).

#### Procedure

Transfer 100 ml.  $\text{NH}_4\text{OAc}$  extract to a 150 ml. beaker and evaporate to dryness. Cool, cover beaker with watchglass and add slowly through lip of beaker 5 ml. conc.  $\text{HNO}_3$  and 1 ml. conc.  $\text{HCl}$ . Warm on hot plate until reaction has subsided and brown fumes are no longer given off. Rinse watchglass into beaker and evaporate contents to dryness at low heat to prevent spattering. Continue to heat for about 10 min. to dehydrate salt. Place beaker in electric muffle furnace at  $150^\circ$  to  $200^\circ\text{C}.$ , heat to  $390^\circ \pm 10^\circ\text{C}.$  and hold at this temperature for 15 min. Remove from muffle and cool. Treat residue with 3 ml.  $\text{HCl}$  (1+1) to dissolve oxides of Mn, Fe and Al, evaporate to dryness at low heat and continue heating for about 30 min. longer to dehydrate silica. Cool. Dissolve residue in 0.1 N  $\text{HNO}_3$ , using rubber policeman to loosen residue. Filter through ashless filter paper into 25 ml. volumetric flask, wash and make to volume with 0.1 N  $\text{HNO}_3$ . Mix thoroughly.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 4. Separation of Mn, Fe, Al and phosphates

#### Note

With strongly acid soils, it is preferable to separate these constituents before determining calcium and magnesium.

#### Reagents

1. Sodium acetate - 10% solution. Dissolve 100 g. NaOAc.  $3\text{H}_2\text{O}$  in water and dilute to 1 liter. Mix thoroughly.
2. Sodium hydroxide - 0.1 N NaOH.
3. Bromine water - Saturated solution of  $\text{Br}_2$  in water.
4. Ammonium chloride - 25% solution. Dissolve 250 g.  $\text{NH}_4\text{Cl}$  in water and dilute to 1 liter. Mix thoroughly.
5. Bromocresol green indicator - as obtained from supply houses.
6. Ammonium hydroxide - 0.6 N  $\text{NH}_4\text{OH}$ .

#### Procedure

Transfer 5 ml. of solution of exchangeable bases in 0.1 N  $\text{HNO}_3$  (Section 3. Treatment of extract) into a 15 ml. centrifuge tube. Add 2 ml. 10% NaOAc solution and mix. Add 1 ml. 0.1 N NaOH and mix. (This solution is buffered at pH 5.7 which is sufficiently high to prevent dissolution of  $\text{MnO}_2$ ). Place in water bath at  $95^\circ\text{C}$ ., add 1 ml. bromine water and mix. Maintain at this temperature for at least 1 hr. to flocculate  $\text{MnO}_2$  and to expel excess  $\text{Br}_2$ . Add 2 ml. 25%  $\text{NH}_4\text{Cl}$  solution and digest for 15 min. longer. Add 1 drop bromocresol green indicator. (If color of indicator persists, complete expulsion of bromine is indicated.) Remove tube from water bath and cool. Add 0.6 N

Procedure (Cont'd)

NH<sub>4</sub>OH until color of solution changes to blue, and then two drops in excess. (Usually 0.5 ml. NH<sub>4</sub>OH is required and may be added at one time.) Dilute to volume of about 11 to 12 ml. with water, mix and digest on waterbath at 80°C. for 5 min. to flocculate precipitate. Centrifuge while hot for 10 min. at 2000 r.p.m. Cool, decant and retain supernatant liquid for Ca and Mg determinations.

Reference (for Sections 1, 2, 3 and 4)

1. Peech, M. et al. Methods of soil analysis for soil-fertility investigations. U.S. Dept. Agr. Circ. 757. 1947.



## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 5. Calcium

#### Reagents

1. Bromocresol green indicator - as obtained from supply houses .
2. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , dilute (1 + 1) and (1 + 25) .
3. Acetic acid -  $\text{HOAc}$ , dilute (1 + 1) .
4. Ammonium oxalate -  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , saturated solution .
5. Sulphuric acid -  $\text{H}_2\text{SO}_4$ , dilute (1 + 4) .
6. Potassium permanganate - standard 0.02 N  $\text{KMnO}_4$  .

#### Procedure

Transfer 5 ml. of solution of exchangeable bases in 0.1 N  $\text{HNO}_3$  (Section 3. Treatment of extract) or supernatant liquid from separation of Mn, Fe, Al and  $\text{PO}_4$  (Section 4) into a 15 ml. centrifuge tube. Add 3 drops bromocresol green indicator, a few drops  $\text{NH}_4\text{OH}$ (1 + 1) to change color to blue, followed by a few drops  $\text{HOAc}$ (1 + 1) to change color to green. (This adjusts reaction of solution to pH 4.6). Add 1.5 ml.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution, mix thoroughly and let stand for at least 1 hr. Centrifuge. Retain supernatant liquid for Mg determination.

Wash precipitate with 5 ml.  $\text{NH}_4\text{OH}$  (1 + 25), breaking it up well. Centrifuge. Drain over filter paper. Dissolve precipitate in 2 ml.  $\text{H}_2\text{SO}_4$  (1 + 4). Heat in beaker of water and titrate with standard  $\text{KMnO}_4$  solution .

1 ml. 0.02 N  $\text{KMnO}_4$  = 0.0004 g. Ca.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 6. Magnesium

#### Reagents

1. Buffer solution - Dissolve 67.5 g.  $\text{NH}_4\text{Cl}$  in about 200 ml. water mixed with 570 ml. conc.  $\text{NH}_4\text{OH}$ . Dilute to 1 liter with water. Mix thoroughly.
2. Potassium cyanide - KCN, 2% aqueous solution.
3. Eriochrome black T indicator solution - Dissolve 0.2 g. Eriochrome black T (Eastman Kodak) in 50 ml.  $\text{CH}_3\text{OH}$  containing 2 g. hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ). (This solution is fairly stable but freshly prepared indicator gives a sharper endpoint.)
4. Standard versenate solution - 0.01 N. Dissolve 4 g. versenate (disodium dihydrogen ethylenediamine tetraacetate) in water containing 0.5 g. NaOH and dilute to 2 liters. Mix thoroughly. Standardize against a standard Mg solution.
5. Standard magnesium solution - Dissolve 1.2325 g.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in water and dilute to 1 liter. Mix thoroughly. This solution is 0.01 N in Mg.

#### Procedure

Transfer supernatant liquid from Ca precipitation to a 250 ml. beaker and dilute to about 150 ml. with water. Add  $\text{NH}_4\text{Cl}$ - $\text{NH}_4\text{OH}$  buffer to adjust to pH 10 (usually about 10 ml. required). Add 1 ml. KCN solution and 6 drops Eriochrome black T indicator solution. Titrate with standard versenate solution using a two-beaker titration procedure. The end-point is from wine-red to blue.

#### References

1. Cheng, K. L. and R. H. Bray. Determination of calcium and magnesium in soil and plant material. Soil Sci. 72: 449-458. 1951.

References (Cont'd)

2. Versenes. Tech. Bul. 2, Bersworth Chemical Co., Framingham,  
Mass. 1953.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 7. Potassium

#### Reagents

1. Internal standard stock solution - 1000 p.p.m. Li. Weigh 9.935 g. oven-dry  $\text{LiNO}_3$  (reagent grade), place in 1 liter volumetric flask and make to volume with water. Mix thoroughly. Store in polyethylene container.
2. Standard potassium solutions:
  - a. Stock solution - 10,000 p.p.m. K. Weigh 19.037 g. oven-dry KCl (reagent grade), place in 1 liter volumetric flask and make to volume with water. Mix thoroughly. Store in polyethylene container.
  - b. Working solution - 1,000 p.p.m. K. Dilute 25 ml. stock solution (10,000 p.p.m. K) to 250 ml. with either neutral normal  $\text{NH}_4\text{OAc}$  solution or 0.1 N  $\text{HNO}_3$ , depending on whether soil extract (Section 1) or prepared solution (Section 3) is being examined. Mix thoroughly. Store in polyethylene container.

#### Procedure

##### a. Preparation of standard curve

Pipette 0, 1, 2, 4, 6 and 8 ml. aliquots of 1000 p.p.m. K solution in appropriate medium into 200 ml. pyrex volumetric flasks. To each add 20 ml internal standard solution (1000 p.p.m. Li) and dilute to volume with appropriate solution (N  $\text{NH}_4\text{OAc}$  or 0.1 N  $\text{HNO}_3$ ). Mix thoroughly. These standards contain 0, 5, 10, 20, 30 and 40 p.p.m. K and 100 p.p.m. Li. Prepare standard curve as described in operating instructions supplied with flame photometer



b. Analysis of soil extract

Pipette 5 ml. internal standard solution (1000 p.p.m. Li) into dry 50 ml. volumetric flask. Dilute to volume with soil extract (Section 1) and mix thoroughly. Atomize in calibrated flame photometer. Record internal standard dial reading. Determine concentration of K in solution from standard curve.

c. Analysis of prepared solution

Pipette 5 ml. prepared solution (Section 3) into dry 50 ml. volumetric flask. Add 5 ml. internal standard solution (1000 p.p.m. Li). Dilute to volume with 0.1 N  $\text{HNO}_3$  and mix thoroughly. Atomize in calibrated flame photometer. Record internal standard dial reading. Determine concentration of K in solution from standard curve.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 8. Sodium

#### Reagents

#### 1. Standard sodium solutions:

- a. Stock solution - 10,000 p.p.m. Na. Weigh 25.415 g. oven-dry NaCl (reagent grade). Place in 1 liter volumetric flask and make to volume with water. Mix thoroughly. Store in polyethylene container.
- b. Working solution - 1000 p.p.m. Na. Dilute 25 ml. stock solution (10,000 p.p.m. Na ) to 250 ml. with either neutral normal  $\text{NH}_4\text{OAc}$  solution or 0.1 N  $\text{HNO}_3$ , depending on whether soil extract (Section 1) or prepared solution (Section 3) is being examined. Mix thoroughly. Store in polyethylene container.

#### Procedure

#### a. Preparation of standard curve

Pipette 0, 2, 4, 6, 8 and 10 ml. aliquots of 1000 p.p.m. Na solution in appropriate medium into 200 ml. pyrex volumetric flasks. Dilute to volume with appropriate solution ( N  $\text{NH}_4\text{OAc}$  or 0.1 N  $\text{HNO}_3$ ). Mix thoroughly. These standards contain 0, 10, 20, 30, 40 and 50 p.p.m. Na. Prepare standard curve as described in operating instructions supplied with flame photometer.

#### b. Analysis of soil extract

Atomize portion of soil extract (diluted with N  $\text{NH}_4\text{OAc}$  if Na concentration is high) in calibrated flame photometer. Record meter readings. Determine concentration of Na in solution from standard curve.

c. Analysis of prepared solution

Pipette aliquot (depending on Na concentration ) of prepared solution (Section 3) into 50 ml. volumetric flask. Dilute to volume with 0.1 N  $\text{HNO}_3$  and mix thoroughly. Atomize in calibrated flame photometer. Record meter readings. Determine concentration of Na in solution from standard curve .

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

### 9. Hydrogen

#### Reagents

1. Ammonium hydroxide - Standard 0.25 N  $\text{NH}_4\text{OH}$ .

#### Procedure

Titrate 100 ml. of  $\text{NH}_4\text{OAc}$  extract (Section 1) with 0.25 N  $\text{NH}_4\text{OH}$  until pH is that of original extracting solution, using titrimeter. ml.  $\text{NH}_4\text{OH}$  x normality factor x 10 = me. H/100 g. soil.

#### Reference

1. Schollenberger, C.J. and R.H. Simon. Determination of exchange capacity and exchangeable bases in soil - ammonium acetate method. Soil Sci. 59: 13-24. 1945.



MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

1. Decomposition of sample with  $\text{Na}_2\text{CO}_3$ ; preparation of solution

Reagents

1. Sodium carbonate -  $\text{Na}_2\text{CO}_3$ , anhydrous .
2. Ethyl alcohol -  $\text{C}_2\text{H}_5\text{OH}$ , 95% .
3. Hydrochloric acid -  $\text{HCl}$ , dilute (60+40), (5+95) and (1+99) .
4. Filtration accelerator .

Procedure

a. Fusion with  $\text{Na}_2\text{CO}_3$  .

Weigh 10 g. anhydrous  $\text{Na}_2\text{CO}_3$ , (A fusion mixture of 4 parts anhydrous  $\text{Na}_2\text{CO}_3$  and 1 part anhydrous  $\text{NaBO}_3$  may be used.) Place about half in Pt crucible and add residue from loss-on-ignition determination (p. 17) . Use all but about 1 g. of remainder of  $\text{Na}_2\text{CO}_3$  to rinse any remaining particles of soil into crucible. Mix thoroughly. Spread remaining 1 g. of  $\text{Na}_2\text{CO}_3$  over mixture .

Support crucible on ring stand several inches above meker burner and cover with Pt lid. Gradually increase heat on crucible by lowering crucible nearer to flame. (When fusion begins, care must be taken to regulate amount of heat to keep spattering at minimum until evolution of gas is complete). Finally heat over full flame (bottom of crucible in hottest zone of flame) of burner for 20 min. , until uniform fused mass is obtained .

Remove lid and rotate hot crucible to distribute fused mass over interior .

b. Dehydration of silica.

Place lid in casserole containing a little water and 1 to 2 ml. 95%  $C_2H_5OH$ . Warm on hot plate at low heat. Partially fill crucible containing melt with warm water, add 2 to 3 ml. 95%  $C_2H_5OH$ , cover with watch glass and digest by supporting crucible in small beaker used as water-bath

Free lid from traces of fusion by treatment with a few ml.  $HCl$  (60+40), followed by hot water, using policeman. With aid of stirring rod (retained in casserole from this point on) transfer disintegrated material from crucible to casserole and repeat digestion until melt is completely transferred. Carefully acidify contents of casserole with  $HCl$  (60+40). Add 20 ml.  $HCl$  (60+40) to crucible, cover and digest on beaker water-bath. Transfer acid from crucible to casserole and thoroughly wash crucible with hot water, using policeman.

Evaporate contents of casserole (covered with watch-glass supported on glass triangle) to dryness on steam bath under conditions where casserole is almost completely surrounded by vapor. Break up any formation of crust with glass rod. When dry, place casserole in oven at  $105^{\circ}C$ . for 1 hr. Remove and cool.

c. Treatment of silica

Using a pipette, moisten contents of casserole with 15 ml.  $HCl$  (60+40), cover with watchglass, let stand for short time, then rapidly bring to boil on hot plate. Add 40 ml. boiling water and thoroughly mix with glass rod. When silica has settled, wash cover glass, triangle and sides of casserole with warm ( $60^{\circ}C$ .) water and filter supernatant liquid through 11 cm Whatman #54 filter paper into

c. Treatment of silica (Cont'd)

400 ml. beaker, retaining as much of silica as possible in casserole. Add 10 ml. water to casserole, stir, decant and repeat this treatment. Add 2 ml. HCl (60+40) taking care to crush lumps in casserole with stirring rod. Finally, using a little water, transfer bulk of precipitate to filter paper.

Add about 3 ml. HCl (5+95) to casserole, scrub casserole and stirring rod with policeman and transfer washings to filter paper with HCl (5+95). Wash filter paper and contents twice with warm (60° C.) water. Transfer filter paper and contents to tared Pt dish and place in oven. (For further treatment, see Section 2 - Silica).

Wash funnel once before transferring filtrate back to original casserole. Place casserole on water bath and take to dryness. Cover with watch-glass and place in oven at 105° C. for 1/2 hr. Remove from oven, cool and, using pipette, moisten contents of casserole with 15 ml. HCl (60+40). Add 25 ml. water containing filtration accelerator, rapidly bring to boil on hot plate and heat for few minutes. When silica has settled, rinse watch glass with HCl (1+99) and filter supernatant liquid through 9 cm. Whatman #40 filter paper into 400 ml. pyrex beaker, retaining as much of silica as possible in casserole. Add 10 ml. HCl (1+99), stir and decant. Using a policeman and HCl (1+99), clean stirring rod thoroughly and transfer contents of casserole to filter paper. Wash casserole with HCl (1+99), using filtration accelerator to collect silica adhering to sides. Wash filter paper 3 or 4 times with HCl (1+99). Transfer filtrate to 500 ml. volumetric flask and keep for analysis, but do not dilute to volume at this stage. (see end of Section 2 - Silica).

## MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

### 2. Silica

#### Reagents

1. Sulphuric acid -  $\text{H}_2\text{SO}_4$ , dilute (1+1).
2. Hydrofluoric acid - HF, 48%.
3. Sodium carbonate -  $\text{Na}_2\text{CO}_3$ , anhydrous (or fusion mixture).
4. Hydrochloric acid - HCl, conc.

#### Procedure

Transfer filter paper containing precipitate from second dehydration to perfectly glazed porcelain crucible, dry in oven and ignite until charred only.

Place tared Pt crucible containing silica from first dehydration in muffle furnace at  $250^\circ\text{C}$ . (Leave door partially open to allow free access of air.) Burn off filter paper and heat to  $600^\circ\text{C}$ . Cool and add charred filter paper containing silica from second dehydration. Ignite combined silica precipitates, first by heating crucible (placed at an angle) over gentle flame until charred filter paper has become white, then covering crucible with Pt lid and heating at full heat for 20 min. Cool in desiccator and weigh. Ignite again for 15 min., cool and weigh. Repeat to constant weight.

Obtain net silica as follows: Treat combined silica precipitates in Pt crucible with 10 ml. water, 5 drops  $\text{H}_2\text{SO}_4$  (1+1), and 10 ml. HF. Heat carefully until only  $\text{H}_2\text{SO}_4$  remains. Cool, add 5 ml. HF and evaporate. Increase heat until all  $\text{SO}_3$  fumes disappear. Place in muffle furnace at  $250^\circ\text{C}$ . and heat to  $750^\circ\text{C}$ . Cool and weigh. Subtract weight of residue from weight of combined silica precipitates to obtain net silica.



Procedure (Cont'd)

Fuse residue from HF treatment with  $\text{Na}_2\text{CO}_3$  or fusion mixture (approx. 0.5 g.). Cool. Digest in water. Carefully acidify with HCl (60+40) and add about 2 ml. in excess. Transfer solution to the 500 ml. volumetric flask containing filtrate from second silica separation (end of Section 1). Dilute to volume and mix thoroughly.

MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

3. Iron

Reagents

1. Hydrochloric acid - HCl, conc., and dilute (1+9) .
2. Standard iron solution - 0.0200 M. Dissolve 1.1181 g. cleaned analyzed iron wire (99.9% Fe) in 20 ml. HCl (1+1) in a 1 liter volumetric flask, warming on water bath until solution is complete. Cool. Dilute to volume with water. Mix thoroughly .
3. Ceric sulphate solution - 0.02 N. Slowly add 30 ml. conc.  $\text{H}_2\text{SO}_4$  to 500 ml. water with constant stirring. Then add 12.6 g. ceric ammonium sulphate dihydrate ( $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ) and stir until solution is complete. Cool, filter if turbid and dilute to 1 liter. Mix thoroughly. Standardize against iron solution (20 ml.) prepared above, according to Procedure given below .
4. O-phenanthroline ferrous sulphate complex - "Ferroin", 0.025 M solution, as obtained from supply houses .

Preparation of silver reductor

Dissolve 29 g.  $\text{AgNO}_3$  in 400 ml. water. Add few drops conc.  $\text{HNO}_3$  and bring to boil. Suspend in it sheet (about 10 cm. square) of electrolytic Cu and stir solution mechanically. Allow reaction to proceed until test shows absence of Ag ions in solution. Wash silver by decantation with  $\text{H}_2\text{SO}_4$  (1+9) until most of Cu has been removed. Place Ag in column similar to, but smaller than, that used for Jones reductor and wash with  $\text{H}_2\text{SO}_4$  (1+9) until test shows absence of Cu in wash liquid .

### Preparation of silver reductor (Cont'd)

With use, dark AgCl coating forms on Ag. When this coating extends downward over 3/4 of length of column, reductor must be regenerated. Fill column with approx. 0.1 M  $\text{H}_2\text{SO}_4$  and insert Zn rod into reductor so that it makes contact with Ag. Reduction proceeds rapidly and, after washing, column is again ready for use.

(Reference: Willard, H.H. and H. Diehl. Advanced quantitative analysis. D. VanNostrand Co. Inc., New York. 1946).

### Procedure

Pipette two 50 ml. aliquots\* prepared solution (end of Section 2), each corresponding to 0.2 g. soil, into 100 ml. beakers. Add 5 ml. conc. HCl, mix and pass solution through Ag reductor at rate of about 20 to 30 ml. per min. (Sometimes suction is required). Collect solution in 500 ml. beaker. Wash Ag 5 or 6 times with 25 ml. portions of HCl (1+9). (When passing solutions through reductor, never allow liquid in column to drain below top of Ag.) Add 10 ml. conc. HCl and titrate immediately with standard ceric sulphate solution using 3 drops o-phenanthroline ferrous sulphate indicator. (Titration may be checked by passing solution through reductor and again titrating.) An indicator blank is obtained by taking equal volume of water, adding 15 ml. conc. HCl and 3 drops of indicator, and titrating to same color change. Calculate per cent  $\text{Fe}_2\text{O}_3$ . 1 ml. 0.02 N ceric sulphate solution = 0.00160 g.  $\text{Fe}_2\text{O}_3$  or 0.00112 g. Fe.

\*Usually only one aliquot need be used for the determination of iron. For samples low in Fe, one 100 ml. aliquot should be used.

## MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

### 4. Titanium

#### Reagents

1. Perchloric acid -  $\text{HClO}_4$ , 72%.
2. Hydrogen peroxide -  $\text{H}_2\text{O}_2$ , 3%.
3. Standard titanium solution - Weigh 2.21 g. recrystallized, air-dried potassium titanium oxalate ( $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ) into 500 ml. kjeldahl flask. Add 8 g.  $(\text{NH}_4)_2\text{SO}_4$  and 50 ml. conc.  $\text{H}_2\text{SO}_4$ . Gradually heat to boiling and boil 10 min. Cool. Pour solution into approx. 750 ml. water. Cool and dilute to 1 liter. Mix thoroughly. 1 ml. contains 0.50 mg.  $\text{TiO}_2$ . (This value can be checked gravimetrically as follows: To a 50 ml. aliquot, add 3 ml. conc.  $\text{H}_2\text{SO}_4$ . Cool. Precipitate Ti with cold 6% solution of cupferron. Wash precipitate thoroughly with  $\text{H}_2\text{SO}_4$  (5+95) containing a little cupferron. Dry and ignite gently until organic matter is destroyed, then strongly to  $\text{TiO}_2$ .)

#### Procedure

Pipette 25 ml. prepared solution (end of Section 2), corresponding to 0.1 g. soil, into 150 ml. beaker. Add 8 ml.  $\text{HClO}_4$  and mix. Cover with "speedy-vap" watch glass and evaporate on hot plate to strong fumes of  $\text{HClO}_4$ . Cool. Transfer to 50 ml. volumetric flask and dilute to approx. 40 ml. Cool. Add 5 ml. 3%  $\text{H}_2\text{O}_2$ , dilute to volume and mix. Determine color intensity in photoelectric colorimeter using blue filter (420-440 mμ) and setting 100% light transmission for a blank prepared by diluting 8 ml.  $\text{HClO}_4$  to 40 ml. in a 50 ml. volumetric flask and adding 5 ml. 3%  $\text{H}_2\text{O}_2$  as above.

Calculate amount of  $\text{TiO}_2$  from a curve prepared as follows: Measure



Procedure (Cont'd)

suitable aliquots (0.25, 0.50, 1.0, 2.0, 4.0 ml.) of standard Ti solution into 50 ml. volumetric flasks. Add 8 ml.  $\text{HClO}_4$ , and proceed as in previous paragraph from where it says ". . . . . dilute to approx. 40 ml. "

MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

5. Combined oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ).

Reagents

1. Filtration accelerator.
2. Bromcresol purple indicator - as obtained from supply houses.
3. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , dilute (1+1).
4. Ammonium nitrate -  $\text{NH}_4\text{NO}_3$ , 2.5% solution.
5. Hydrochloric acid -  $\text{HCl}$ , conc.

Procedure

Transfer remainder of prepared solution (end of Section 2), 375 ml., corresponding to 1.5 g. soil, to 600 ml. beaker. Reduce volume to about 300 ml. and add filtration accelerator (except for complexometric determination - see Section 10). Heat on hot plate to  $80^\circ$  to  $90^\circ \text{C}$ . Add 10 drops bromcresol purple indicator. From a burette add  $\text{NH}_4\text{OH}$  (1+1) with constant stirring until solution has turned purple, then 5 drops in excess. Keep warm on hot plate. Should yellow color develop, add 4 drops  $\text{NH}_4\text{OH}$  (1+1) to restore alkalinity.

Transfer beaker to asbestos gauze on tripod over bunsen burner and, while stirring to avoid bumping, bring to boil and boil for 30 sec. Maintain alkalinity by adding  $\text{NH}_4\text{OH}$  (1+1) as required. Set aside and let stand few min before filtering. If purple color of supernatant liquid fades, restore by adding 4 drops  $\text{NH}_4\text{OH}$  (1+1). Filter through 12.5 cm. Whatman #41 filter paper into 800 ml beaker. Use hot 2.5%  $\text{NH}_4\text{NO}_3$  solution (adjusted to slight purple color, using bromcresol purple indicator) to transfer precipitate to filter paper. Wash precipitate free from sides of filter paper and three times more. (Filtrate is

Procedure (Cont'd)

used for determination of Ca and Mg (Sections 6 and 7) and may be concentrated while next step is being carried out.)

Transfer filter paper and precipitate back to original beaker and macerate. Add 12 to 15 ml. conc. HCl, and dilute to about 200 ml. Heat to 80° to 90° C. on hot plate, add 10 drops bromcresol purple indicator and  $\text{NH}_4\text{OH}$  (1+1) with constant stirring until faint purple color has been attained. Then, as above, boil over bunsen burner for 30 sec., set aside and see that supernatant liquid has the proper reaction, and filter through 15 cm. Whatman #41 filter paper into beaker containing solution from first precipitation of oxides. Transfer precipitate completely to filter paper using policeman and some filtration accelerator and wash 8 to 10 times with hot ammoniacal 2.5%  $\text{NH}_4\text{NO}_3$  solution.

Continue evaporation of combined filtrates to 250 ml. prior to precipitation of Ca; maintain slightly alkaline reaction by addition of few drops  $\text{NH}_4\text{OH}$  (1+1) if necessary. If  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  separate out add small amount of filtration accelerator, filter through 9 cm. Whatman #41 filter paper, wash with hot 2.5%  $\text{NH}_4\text{NO}_3$  solution and add precipitate to main one

Transfer precipitate to tared Pt crucible and dry in oven. Place crucible in muffle furnace at low temperature to burn off filter paper. Leave door partially open to allow free access of air. Increase temperature gradually to 800 to 900°C. and maintain there for 1 hr. Remove crucible, cool and weigh. Reignite, cool and weigh. Calculate per cent combined oxides.

Procedure (Cont'd)

Calculate per cent  $\text{Al}_2\text{O}_3$  by subtracting per cent  $\text{Fe}_2\text{O}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5$  from per cent combined oxides .

## MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na) TOTALS

### 6. Calcium

#### Reagents

1. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , dilute (1+1).
2. Hydrogen sulphide -  $\text{H}_2\text{S}$ , gas, and aqueous solution made distinctly ammoniacal.
3. Ammonium oxalate -  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , saturated solution.
4. Hydrochloric acid -  $\text{HCl}$ , conc. and dilute (1+4).
5. Sulphuric acid -  $\text{H}_2\text{SO}_4$ , 4 N solution.
6. Standard potassium permanganate solution - 0.05 N  $\text{KMnO}_4$ .

#### Procedure

Evaporate combined filtrates from oxide precipitations (previous section) to about 200 ml. Transfer to 250 ml. erlenmeyer flask, add 3 ml.  $\text{NH}_4\text{OH}$  (1+1) and saturate with  $\text{H}_2\text{S}$  gas. (Mn, Zn, Ni, Co, Cu, and some of Pt contamination from crucible, are precipitated.) Add 3 ml.  $\text{NH}_4\text{OH}$  (1+1), fill flask, stopper and let stand overnight. Filter rapidly, using a little filter accelerator, into 400 ml. beaker and immediately wash twice with 10 ml. portions of aqueous solution of  $\text{H}_2\text{S}$  made distinctly ammoniacal. Heat to boiling and, while stirring, slowly add 15 ml. saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Cover, boil for 1 min. and place on waterbath for 1 hr. Let cool. Filter (Whatman No. 40) into 600 ml. beaker and wash twice with cold ammoniacal water. Filtrate is used for Mg determination.

Wash precipitate (filter paper retained in partially inverted funnel) back into the 400 ml. beaker, using cold water. Wash sides of beaker with



Procedure (Cont'd)

hot HCl (1+4). Add 2 ml. conc. HCl and bring to boil. Add 10 ml. saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution (no precipitate should form at this point) and, while boiling, slowly add  $\text{NH}_4\text{OH}$  (1+1) from burette until alkaline. Digest at  $80^\circ$  to  $90^\circ\text{C}$ . for 1/2 to 1 hr. Filter through original filter paper and wash thoroughly with cold slightly ammoniacal water. Add this filtrate to previous one for determination of Mg.

Pierce apex of filter paper and wash precipitate with cold water into beaker in which precipitation was made. Dissolve precipitate in hot 4 N  $\text{H}_2\text{SO}_4$ , rinsing sides of beaker. Titrate while hot with standard 0.05 N  $\text{KMnO}_4$  solution. Add filter paper, wash funnel and complete titration.

1 ml. 0.05 N  $\text{KMnO}_4$  = 0.001 g. Ca or 0.0014 g.  $\text{CaO}$ .

## MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na) TOTALS

### 7. Magnesium

#### Reagents

1. Diammonium phosphate -  $(\text{NH}_4)_2\text{HPO}_4$ , 20% solution.
2. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , conc. and dilute (1+19).
3. Hydrochloric acid -  $\text{HCl}$ , dilute (1+4).

#### Procedure

Combine filtrates from calcium precipitations (amounting to about 400 ml.) in 600 ml. beaker and make slightly acid. Add 10 ml. 20% diammonium phosphate solution for each 100 ml. solution and stir. Add conc.  $\text{NH}_4\text{OH}$  in small increments and at intervals and stir vigorously without touching sides of beaker. When precipitate has definitely formed, add 15 to 20 ml. conc.  $\text{NH}_4\text{OH}$  in excess and let stand overnight. Filter (15 cm. Whatman No. 42) and wash several times with  $\text{NH}_4\text{OH}$  (1+19).

Wash precipitate back into original beaker with ammoniacal water. Wash sides of beaker with  $\text{HCl}$  (1+4) using enough to make solution acid. Warm, pour through original filter paper into 250 ml. beaker and wash with hot acidified water to about 180 ml. Complete determination by either (a) or (b) below.

(a) Evaporate to 75 ml. and cool. Add 3 to 4 ml. 20%  $(\text{NH}_4)_2\text{HPO}_4$  solution, followed by conc.  $\text{NH}_4\text{OH}$  very carefully until a precipitate is formed. Finally add 7 ml. in excess. Let stand overnight. Filter through weighed Pt gooch crucible, wash with cold  $\text{NH}_4\text{OH}$  (1+19), dry, ignite, and weigh as  $\text{Mg}_2\text{P}_2\text{O}_7$ . Report as  $\text{MgO}$ .  $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.3623 = \text{MgO}$ .

Procedure (Cont'd)

(b) Cool, transfer to 200 ml. volumetric flask, dilute to volume and mix.

Titrate appropriate aliquot with EDTA as for exchangeable Mg (p. 36) .

MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

8. Potassium and sodium

Reagents

1. Ammonium chloride -  $\text{NH}_4\text{Cl}$  .
2. Calcium carbonate -  $\text{CaCO}_3$ , alkali-free .
3. Ammonium carbonate -  $(\text{NH}_4)_2\text{CO}_3$ , saturated solution .
4. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , conc.
5. Ammonium oxalate -  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , saturated solution .
6. Nitric acid -  $\text{HNO}_3$ , 0.1 N .

Procedure

Weigh 0.5 g. 100-mesh soil, 0.5 g.  $\text{NH}_4\text{Cl}$  and 4 g.  $\text{CaCO}_3$  (alkali-free) and mix thoroughly in glass mortar .

Transfer to Pt crucible containing layer of  $\text{CaCO}_3$  in bottom. Rinse mortar with little  $\text{CaCO}_3$  and add to surface of material in Pt crucible. Place crucible in hole in asbestos board so that about half of it projects through. Heat gradually until ammonia fumes have been completely driven off. Apply full heat of meker burner and keep lower half of crucible (covered) at bright red heat for 20 to 30 min .

Transfer fused mass to porcelain evaporating dish (about 3-1/2 in. in diam.), cover and slake with hot water. Grind with agate pestle, followed by decantation (through S & S 589 -11 cm. filter paper) into 600 ml. beaker. Add more water, grind and decant, and repeat 2 to 3 times until all is ground and dispersed. Wash with hot water until filtrate is about 300 ml.

Procedure (Cont'd)

Precipitate lime with 10 ml. saturated  $(\text{NH}_4)_2\text{CO}_3$  solution plus 5 to 6 drops conc.  $\text{NH}_4\text{OH}$ , cover, bring to boil and allow to settle. Filter into 400 ml. beaker and evaporate to 10 ml. Add 1 ml. saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and few drops conc.  $\text{NH}_4\text{OH}$ . If precipitate forms, filter. Evaporate to dryness and heat in muffle furnace at  $400^\circ\text{C}$ . to drive off ammonia fumes. Take up with 10 ml. 0.1 N  $\text{HNO}_3$  and filter into 100 ml. volumetric flask. Wash with 0.1 N  $\text{HNO}_3$ . Dilute to volume and mix thoroughly. (For other than immediate analysis, store in polyethylene bottle.)

Using suitable aliquots, determine potassium and sodium by procedures given for exchangeable cations (pp. 38-40).



MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

9. Decomposition of sample with HF and H<sub>2</sub>SO<sub>4</sub>; preparation of solution.

Reagents

1. Sulphuric acid - H<sub>2</sub>SO<sub>4</sub>, dilute (1+1) .
2. Hydrofluoric acid - HF, 48% .
3. Nitric acid - HNO<sub>3</sub>, conc .
4. Hydrochloric acid - HCl, dilute (1+1) .

Procedure

Weigh 1.000 g. 100-mesh soil into 100 ml. Pt dish. Heat to 500°C. in muffle furnace and maintain for 1/2 hr. Cool. Moisten with 2 ml. water and 5 ml. H<sub>2</sub>SO<sub>4</sub> (1+1) and mix. Add 10 ml. HF and mix by rotation. Place on asbestos mat or perforated metal sheet over hot plate and gradually increase heat. (If sludge tends to adhere to bottom of dish, loosen by stirring with small teflon rod.) Continue heating (avoid boiling because spattering may occur) until SO<sub>3</sub> fumes appear. Cool. Wash down sides of dish with little water and add 10 ml. HF. Repeat evaporation until SO<sub>3</sub> fumes evolve. Place dish over electric heater or gas burner and heat to strong SO<sub>3</sub> fumes but not to dryness. Cool. Add 3 ml. H<sub>2</sub>SO<sub>4</sub> (1+1), (running it down sides of dish) and 1 ml. conc. HNO<sub>3</sub>. Wash down sides of dish with little water and again heat to copious SO<sub>3</sub> fumes. Repeat last treatment. Dish should now contain 2 to 3 ml. H<sub>2</sub>SO<sub>4</sub>. Prepare solution for analysis by one of following methods:

(a) Cool dish and contents. Carefully add 50 to 60 ml. water, cover and digest for 1/2 hr. on water bath. If more than very small residue remains, transfer solution and residue to 400 ml. Vycor beaker and boil gently for 15

### Procedure (Cont'd)

min. Filter into 250 ml. volumetric flask, dilute to volume and mix thoroughly.

(b) Continue driving off  $\text{SO}_3$  almost to dryness. Avoid local over-heating lest Al be converted to insoluble form. Place dish on triangle in muffle furnace at  $330^\circ\text{C}$ . until  $\text{SO}_3$  fumes just cease to evolve. Cool. Add 20 ml. HCl (1+1) and digest on water bath to dissolve salts. Cool. Filter solution into 250 ml. volumetric flask, retaining any residue in dish. Add 2 to 3 ml. HCl (1+1) to dish, heat and transfer solution to flask. Repeat if necessary. Cool solution in flask, dilute to volume and mix thoroughly.

Solution prepared under (a) or (b) can be used for determination of Fe, Al, Ti, Mn, Ca, Mg, K and Na. Solution prepared under (a) may be used for determination of P as well.

### References

1. Fieldes, M., L. D. Swindale, J. P. Richardson and I. C. McDowall. Rapid method for analysis of soil clays and other silicates. New Zealand J. Sci. Tech. 35B: 433-439. 1954.
2. Hillebrand, W. F., G. E. F. Lundell, H. A. Bright and J. I. Hoffman. Applied inorganic analysis. John Wiley and Sons, New York. 1953.
3. Shapiro, L. and W. W. Brannock. Rapid analysis of silicate rocks. U.S. Geol. Survey Bull. 1036-C. 1956.

MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

10. Iron and Aluminum (complexometric, tentative)

Reagents

1. Ascorbic acid.
2. Buffer solution - Dissolve 300 g.  $\text{NH}_4\text{OAc}$  in water, dilute to 500 ml., mix and adjust to pH 6.8 to 7.0.
3. Thioglycollic acid solution - Dilute 10 ml. thioglycollic acid to 100 ml. with water. Mix thoroughly. Store in dark bottle. Renew every week.
4. Ammonium fluoride solution - Dissolve 50 g.  $\text{NH}_4\text{F}$  in water, dilute to 500 ml. in polyethylene bottle and mix. Adjust to pH 6.5.
5. Ethyl alcohol -  $\text{C}_2\text{H}_5\text{OH}$ , 95%.
6. Ammonium hydroxide -  $\text{NH}_4\text{OH}$  (1+4).
7. Hydrochloric acid -  $\text{HCl}$  (1+7).
8. Standard iron solution - 0.0200 M. Dissolve 1.1181 g. cleaned iron wire (99.9% Fe) in 20 ml.  $\text{HCl}$  (1+1) in a 1 liter volumetric flask, warming on water bath until solution is complete. Cool. Dilute to volume with water. (Avoid excess  $\text{HCl}$  because solution more acid than about 0.1 N is undesirable.) Mix thoroughly.
9. Standard EDTA solution - 0.0200 M. Dissolve 8.0 g. disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA) in water and dilute to 1 liter. Mix thoroughly. Withdraw 50 ml. and use this to determine molarity by titrating duplicate 10 ml. aliquots of standard Fe solution. Dilute remaining 950 ml. EDTA solution to give molarity of exactly 0.0200. Mix thoroughly. Check by duplicate titration. For prolonged storage, use polyethylene bottle.

## Apparatus

- 1a. Magnetic stirrer and stirring bar.
- 1b. pH meter with long lead 5-inch calomel and glass electrodes
- or:
- 2. Automatic titration apparatus

## Procedure

Prepare solution of combined oxides in 250 ml. of approx. 1.0 N HCl according to Procedure under Section 5 with three exceptions: (1) omit addition of filtration accelerator (para. 1); (2) use Whatman #41A, rather than #41, filter paper (para. 2); (3) do not macerate filter paper with precipitate (para. 3); instead, partially invert funnel and wash precipitate as completely as possible back into original beaker. (Solution of soil constituents may be obtained as directed under either Section 1 or Section 9. Double precipitation of oxides is unnecessary unless Ca and Mg are to be determined subsequently.)

- a. Iron. Transfer suitable aliquot (equivalent to 3 to 15 mg.  $\text{Fe}_2\text{O}_3$ ) of prepared solution to 400 ml. tall-form beaker. Add small amount (approx. 0.2 g.) ascorbic acid and 15 ml. buffer solution. Dilute to approx. 150 ml. with water. Add 3 ml. thioglycollic acid solution, 5 ml.  $\text{NH}_4\text{F}$  solution and 25 ml.  $\text{C}_2\text{H}_5\text{OH}$ . Carefully adjust to pH 6.5 with  $\text{NH}_4\text{OH}$  (1+4), using pH meter and magnetic stirrer. Titrate with standard EDTA solution against white background, using magnetic stirrer at speed to form vortex half the depth of liquid, until red-violet color just disappears. (As color fades on approaching end-point, allow sufficient time between additions of titrant to establish equilibrium and thus prevent overtitration.)

Procedure (Cont'd)

ml. EDTA x molarity = millimoles Fe in aliquot

millimoles Fe x 79.85 = mg.  $\text{Fe}_2\text{O}_3$

- b. Iron and aluminum. Transfer suitable aliquot (equivalent to 5 to 30 mg. combined oxides) of prepared solution to 400 ml. tall-form beaker. Add small amount (approx. 0.2 g.) ascorbic acid and a carefully measured amount of EDTA solution sufficient to chelate Fe, Al and Ti and provide excess of 10 to 25%. (Each 1.6 mg.  $\text{Fe}_2\text{O}_3$  or 1.0 mg.  $\text{Al}_2\text{O}_3$  or 1.6 mg.  $\text{TiO}_2$  requires 1 ml. 0.0200 M EDTA solution. Amount required for Fe is known from iron determination above.) Dilute to approx. 125 ml. and adjust to pH 6.1 to 6.3. Boil 2 min. and cool to room temp. Add small amount (approx. 0.1 g.) ascorbic acid, 15 ml. buffer solution, 3 ml. thioglycollic acid solution and 25 ml.  $\text{C}_2\text{H}_5\text{OH}$ . Carefully adjust to pH 6.5 using pH meter and magnetic stirrer. Warm to about 35°C. and back-titrate with standard Fe solution, stirring as in Fe determination. (Run titrant into vortex of liquid.) End-point is reached when faint pink color persists for at least 15 sec. Immediately add 5 ml.  $\text{NH}_4\text{F}$  solution and, after 1 to 2 min., continue back-titration until faint pink color reappears. (This takes care of  $\text{TiO}_2$  and usually does not require more than an additional 1 ml. of titrant.)

(ml. EDTA x molarity) - (ml. std. Fe x molarity) = millimoles

Fe+Al in aliquot

millimoles Fe+Al - millimoles Fe = millimoles Al

millimoles Al x 50.98 = mg.  $\text{Al}_2\text{O}_3$ .



## MAJOR CONSTITUENTS (Si, Fe, Ti, Al, Ca, Mg, K, Na), TOTALS

### 11. Iron, aluminum and titanium (complexometric, tentative)

#### Reagents

1. All reagents given under Section 10 .
2. Sulphuric acid -  $\text{H}_2\text{SO}_4$  (1+1) .
3. Hydrogen peroxide -  $\text{H}_2\text{O}_2$ , 3% .

#### Procedure

Prepare solution of combined oxides in 250 ml. of approx. 1 N HCl according to Procedure under Section 5 as modified in Section 10. (Solution of soil constituents may be obtained as directed under either Section 1 or Section 9. Double precipitation of oxides is unnecessary unless Ca and Mg are to be determined subsequently.) Pipette aliquot representing 200 to 400 mg. soil into 100 ml. beaker. (If volume exceeds 40 ml. reduce by evaporation.) Add 3 ml. thioglycollic acid solution. Adjust to pH 2.2 using pH meter. Wash contents of beaker into 60 ml. centrifuge tube. Place in hot water bath until Ti precipitate forms a floc (20 to 30 min.). Centrifuge, cool, decant supernatant liquid and divide into two equal parts. Retain precipitate .

- a. Iron. Transfer half of supernatant liquid to 400 ml. tall-form beaker. Proceed as directed in Section 10, Procedure, a. Iron, from where it says "Add small amount (approx. 0.2 g.) ascorbic acid . . . . .", using however, only 1.5 ml. thioglycollic acid solution. (If Fe in aliquot is too low,  $< 3$  mg.  $\text{Fe}_2\text{O}_3$ , more than half the supernatant liquid will have to be used. In that event, amount of thioglycollic acid solution will have to be reduced so that total amount present will be 3 ml.) .

Procedure (Cont'd)

- b. Iron and aluminum. Transfer remainder of supernatant liquid to 400 ml. tall-form beaker. Proceed as directed in Section 10, Procedure, b. Iron and aluminum, from where it says "Add small amount (approx. 0.2 g.) ascorbic acid . . . ." down to " . . . persists for at least 15 sec.", bearing in mind that Ti has been removed from solution.
- c. Titanium. Dissolve  $\text{TiO}_2$  precipitate in centrifuge tube in 20 ml.  $\text{H}_2\text{SO}_4$  (1+1). Transfer to 100 ml. volumetric flask, add 10 ml. 3%  $\text{H}_2\text{O}_2$  and dilute to volume. Mix thoroughly. (If amount of  $\text{TiO}_2$   $>4$  mg., increase final volume, maintaining same concentrations of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ .) Determine color intensity as directed under Section 4, Titanium.

MINOR CONSTITUENTS (Mn, Cu, Co, Zn, Pb), TOTALS

1. Decomposition of sample

Reagents

1. Perchloric acid -  $\text{HClO}_4$ , approx. 72% .
2. Nitric acid -  $\text{HNO}_3$ , conc., distilled .
3. Hydrofluoric acid -  $\text{HF}$ , approx. 49% .
4. Distilled water - redistilled from pyrex glass still .
5. Hydrochloric acid - distilled (constant boiling)  $\text{HCl}$  , approx. 6.2 N .

Procedure

Digest 2 g. of 200-mesh material (See "Preparation of sample", p. 13) in a covered beaker with 10 ml.  $\text{HClO}_4$  and 15 ml.  $\text{HNO}_3$  until solution is white and all  $\text{HNO}_3$  has been driven off. Transfer to Pt dish, add 10 ml.  $\text{HF}$ , and evaporate almost to dryness. Again add 10 ml.  $\text{HF}$  and about 10 ml. water, washing sides of dish well. Evaporate to dryness or until a brown spot shows on bottom of dish. Cool and add 16 ml. 6.2 N  $\text{HCl}$  to dissolve residue. Transfer to 100 ml. volumetric with hot water. Cool and dilute to volume. Mix thoroughly .

## MINOR CONSTITUENTS (Mn, Cu, Co, Zn, Pb), TOTALS

### 2. Manganese

#### Reagents

1. Nitric acid -  $\text{HNO}_3$ , conc., distilled.
2. Phosphoric acid solution - Dilute 4.5 ml. 85%  $\text{H}_3\text{PO}_4$  to 50 ml.
3. Distilled water - redistilled and containing 5 drops 85%  $\text{H}_3\text{PO}_4$  and a few grains of  $\text{KIO}_4$  per liter. Boil and cool.
4. Standard manganese solution - Dissolve 0.2876 g. freshly ground and dried  $\text{KMnO}_4$  in 20 ml. water. Reduce  $\text{KMnO}_4$  with 0.1 N oxalic acid solution in presence of sufficient  $\text{H}_2\text{SO}_4$ . Make to 1 liter. Mix thoroughly.  
1 ml. = 0.1 mg. Mn.

#### Procedure

Transfer a 25 ml. aliquot of prepared solution (Section 1, Procedure) corresponding to 0.5 g. soil, to 250 ml. beaker and evaporate to dryness. Drive off all chlorides by three successive additions of 5 ml. conc.  $\text{HNO}_3$ , taking to dryness on water bath after each addition. Add 50 ml.  $\text{H}_3\text{PO}_4$  solution (containing 4.5 ml. 85%  $\text{H}_3\text{PO}_4$ ), boil to dissolve all salts, then cool. Add 0.4 g.  $\text{KIO}_4$ , boil for 3 minutes on hot plate, then let stand on hot water bath for 30 min. Cool and dilute to 100 ml. with the distilled water containing  $\text{H}_3\text{PO}_4$  and  $\text{KIO}_4$ . Mix thoroughly. Determine color intensity with photoelectric colorimeter using green (#54) filter and setting 100% light transmission for a blank. (Any cloudiness in solution must be removed by centrifuging before reading is made in colorimeter.)

Calculate amount of Mn from a curve prepared as follows: Measure

### Procedure (Cont'd)

suitable aliquots (containing 0.05 to 1.00 mg. Mn) from standard solution into 250 ml. beakers, evaporate to dryness and proceed as in previous paragraph from where it says: "Drive off all chlorides . . . . ". Express as p.p.m. air-dried soil.

### References

1. Piper, C.S. Soil and plant analysis. Interscience Publishers Inc., New York. 1944.
2. Willard, H.H. and L.H. Greathouse. Colorimetric determination of manganese by oxidation with periodate. J. Am. Chem. Soc. 39: 2366-2377. 1917.



## MINOR CONSTITUENTS (Mn, Cu, Co, Zn,Pb), TOTALS

### 3. Separation of Cu and of Co from Zn and Pb

#### Reagents

1. Ammonium citrate buffer - Dissolve 225 g.  $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$  in 1 liter redistilled water in large separatory funnel. Add 40 to 45 ml. conc.  $\text{NH}_4\text{OH}$  to pH 8.5. Purify by repeated extractions with dithizone reagent (see below) and remove excess dithizone by repeated extraction with pure carbon tetrachloride ( $\text{CCl}_4$ ).
2. Dithizone solution - Dissolve 0.25 g. diphenylthiocarbazone in 500 ml.  $\text{CCl}_4$  in 4-liter separatory funnel. After standing for 15 min. with frequent shaking, add 2 liters 0.02 N  $\text{NH}_4\text{OH}$  and extract dithizone into aqueous phase by vigorous shaking. Discard  $\text{CCl}_4$  phase and extract ammoniacal solution of dithizone with 50 ml. portions of  $\text{CCl}_4$  until  $\text{CCl}_4$  is pure green colour. Discard  $\text{CCl}_4$  phase after each extraction. Add 250 ml.  $\text{CCl}_4$  and 50 ml. N HCl and shake to transfer dithizone into  $\text{CCl}_4$  phase. Dilute  $\text{CCl}_4$  dithizone solution to 1 liter with  $\text{CCl}_4$  and store in black painted pyrex bottle.
3. Thymol blue indicator - Dissolve 0.1 g. thymol blue in 20 ml. hot water and dilute to 100 ml. with 95%  $\text{C}_2\text{H}_5\text{OH}$ . Mix.
4. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , distilled, approx. 6 N.
5. Hydrochloric acid - 0.02 N HCl, prepared from distilled (constant boiling) HCl.
6. Carbon tetrachloride -  $\text{CCl}_4$ .

#### Procedure

- (a) Transfer 50 ml. of prepared solution (Section 1, Procedure)

Procedure (Cont'd)

(equivalent to 1 g. soil) to 125 ml. separatory funnel. Add 5 ml. ammonium citrate buffer solution and 5 drops thymol blue indicator. Titrate with re-distilled ammonia until red colour passes through brownish yellow to yellow. Adjust to pH 2.5, using pH meter.

(b) Add 10 ml. dithizone solution and shake for 5 min. Allow phases to separate. Transfer  $\text{CCl}_4$  (dithizone) phase to clean funnel. Repeat extraction\*, using 5 ml. dithizone solution until last extract is distinct clear green. Save dithizone extractions for Cu determination. (Co remains in aqueous phase with Zn and Pb.)

(c) To aqueous phase add 5 ml. ammonium citrate buffer solution and 5 drops thymol blue indicator and titrate with redistilled ammonia until colour changes from orange to greenish blue. Adjust to pH 8.5, using pH meter.

(d) Add 10 ml. dithizone solution and shake for 2 min. Allow phases to separate and draw off  $\text{CCl}_4$  (dithizone) phase into second separatory funnel. Repeat extraction\* with dithizone solution until last extract is distinct clear green. Combine dithizone extracts in second funnel and discard aqueous phase.  $\text{CCl}_4$  phase will now contain Co, Zn and Pb.

(e) To combined dithizone extracts pipette 25 ml. 0.02 N HCl and shake for 2 min. Draw off  $\text{CCl}_4$  phase into second funnel. Repeat extractions with 25 ml. 0.02 N HCl and draw off  $\text{CCl}_4$  phase which contains Co into 100 ml. beaker. Save for Co determination. Combine the two acid extracts in second funnel and wash three times with 4 to 5 ml.  $\text{CCl}_4$ , running  $\text{CCl}_4$  wash-

Procedure (Cont'd)

ings into the 100 ml. beaker. Save combined acid extracts for determination of Zn and Pb.

\*When two or more extractions are made, dithizone solution may be diluted as required.

Reference

1. Holmes, R.S. Determination of total copper, zinc, cobalt and lead in soils and soil solutions. Soil Sci. 59: 77-84. 1945.

## MINOR CONSTITUENTS (Mn, Cu, Co, Zn, Pb), TOTALS

### 4. Copper

#### Reagents

1. Nitric acid -  $\text{HNO}_3$ , conc. distilled.
2. Perchloric acid -  $\text{HClO}_4$ , approx. 72%.
3. Hydrochloric acid - 1.0 N  $\text{HCl}$ , prepared from distilled (constant boiling)  $\text{HCl}$ .
4. Phenolphthalein indicator - Dissolve 0.1 g. phenolphthalein in 100 ml. 95%  $\text{C}_2\text{H}_5\text{OH}$ .
5. Ammonium hydroxide -  $\text{NH}_4\text{OH}$ , distilled.
6. Carbamate solution - Dissolve 0.2 g. sodium diethyl dithiocarbamate in 100 ml. water, filter into separatory funnel and shake with 5 ml. portions of  $\text{CCl}_4$  to remove copper. Prepare fresh solution for each use.
7. Carbon tetrachloride -  $\text{CCl}_4$ .
8. Standard copper solution - Dissolve exactly 0.1 g. electrolytic copper in 10 ml. dil.  $\text{HNO}_3$ . Evaporate solution almost to dryness, add 2 to 3 drops glacial  $\text{HOAc}$  and make to 1 liter. Mix thoroughly. 1 ml. = 0.1 mg. Cu. A more convenient working standard is prepared by diluting this solution to a concentration of 0.001 mg. Cu per ml.

#### Procedure

Transfer copper dithizonate (Section 3, Procedure, para. b) quantitatively to 50 ml. beaker, add 0.5 ml. redistilled  $\text{HNO}_3$  and 0.7 ml.  $\text{HClO}_4$ . Cover with watch glass, evaporate and fume well until approx. 0.5 ml.  $\text{HClO}_4$  remains. Cool, add 10 ml. water and boil to remove traces of  $\text{HNO}_3$ . Trans-

Procedure (Cont'd)

fer solution from beaker to separatory funnel using hot N HCl to approx. 25 ml. Add 2 to 3 drops phenolphthalein and titrate with redistilled ammonia to very faint pink colour. Adjust to pH 8.5 using pH meter. Add 5 ml. purified carbamate solution and exactly 10 ml.  $\text{CCl}_4$  and shake for 3 min. Allow phases to separate and draw off  $\text{CCl}_4$  phase through loose pledget of cotton placed in stem of separatory funnel. Determine color intensity with photo-electric colorimeter using blue (#42) filter and setting 100% light transmission for pure  $\text{CCl}_4$  (not the blank).

Calculate amount of Cu from curve prepared as follows: Measure suitable aliquots (containing 0.001 to 0.020 mg. Cu) from standard solution into 100 ml. beakers, add 0.5 ml. redistilled  $\text{HNO}_3$  and proceed in exactly the same manner as for unknown (see previous paragraph). Express as p.p.m. air-dried soil.



## MINOR CONSTITUENTS (Mn, Cu, Co, Zn, Pb), TOTALS

### 5. Cobalt

#### Reagents

1. Nitric acid -  $\text{HNO}_3$ , conc., distilled.
2. Perchloric acid -  $\text{HClO}_4$ , approx. 72%.
3. Distilled water - 10 ml. containing 0.5 ml. constant boiling  $\text{HCl}$  and 0.5 ml. 10%  $\text{HNO}_3$ .
4. Nitroso-R-salt - 0.1% aqueous solution.
5. Sodium acetate -  $\text{NaOAc}$ , anhydrous.
6. Standard cobalt solution - Dehydrate 5 g.  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in electric oven at  $250^\circ\text{C}$ . to  $300^\circ\text{C}$ . to constant weight. Weigh exactly 0.263 g., place in liter volumetric flask, dissolve in 50 ml. water and 1 ml.  $\text{H}_2\text{SO}_4$  and dilute to volume. Mix thoroughly. 1 ml. = 0.1 mg. Co. A more convenient working standard is prepared by diluting this solution to concentration of 0.001 mg. Co per ml.

#### Procedure

To 100 ml. beaker containing Co (Section 3, Procedure, para. e) add 0.5 ml. conc.  $\text{HNO}_3$  and 3 ml.  $\text{HClO}_4$ . Evaporate at low heat on hot plate to dryness and drive off remaining  $\text{HClO}_4$  in muffle furnace at  $300^\circ\text{C}$ .

Take up residue in 10 ml. water containing 0.5 ml. constant boiling  $\text{HCl}$  and 0.5 ml. 10%  $\text{HNO}_3$ . Boil for few minutes until volume approximates 7 ml. Add 2 ml. 0.1% solution nitroso-R-salt and 2 g. anhydrous  $\text{NaOAc}$ . (Reaction of resulting solution should be approx. pH 5.5). Boil for 45 sec., add 1.5 ml. conc.  $\text{HNO}_3$  and boil for another 45 sec. Cool rapidly in ice

Procedure (Cont'd)

bath and store in dark place for 20 min. Wash into 25 ml. volumetric flask and dilute to volume. Mix thoroughly. Determine color intensity with photoelectric colorimeter using green (# 54) filter and setting 100% light transmission for blank (not water) .

Calculate amount of Co from curve prepared as follows: Measure suitable aliquots (containing 0.005 to 0.020 mg. Co) from standard solution into 100 ml. beakers, add 1 ml. conc.  $\text{HNO}_3$  and evaporate to dryness. Proceed in exactly the same manner as for unknown (see previous paragraph) from where it says "Take up residue in 10 ml. water . . . . . " Express as p.p.m. air-dried soil .

Reference

1. McNaught, K.J. The determination of cobalt in animal tissues.  
Analyst 67: 97-98. 1942.

## MINOR CONSTITUENTS (Mn, Cu, Co, Zn, Pb), TOTALS

### 6. Zinc

#### Reagents

1. Hydrochloric acid - 0.02 N HCl, prepared from constant boiling HCl.
2. Ammonium citrate buffer - see under Section 3. Separation of Cu, etc.
3. Phenolphthalein indicator - Dissolve 0.1 g. phenolphthalein in 100 ml. 95% C<sub>2</sub>H<sub>5</sub>OH.
4. Dithizone reagent - see under Section 3. Separation of Cu, etc.
5. Carbamate reagent - see under Section 4. Copper.
6. Ammonium hydroxide - 0.01 N NH<sub>4</sub>OH.
7. Standard zinc solution - Weigh exactly 0.1 g. pure Zn, place in liter volumetric flask, dissolve in mixture of 50 ml. water and 1 ml. conc. H<sub>2</sub>SO<sub>4</sub> and dilute to volume. Mix thoroughly. 1 ml. = 0.1 mg. Zn. A more convenient working standard is prepared by diluting this solution to concentration of 0.001 mg. Zn per ml.

#### Procedure

From separatory funnel containing 0.02 N HCl extract (Section 3, Procedure, para. e) take suitable aliquot equivalent to 0.1 to 0.2 g. soil. Place aliquot in clean separatory funnel and dilute to 25 ml. volume with 0.02 N HCl. Add 5 ml. ammonium citrate buffer and titrate, using phenolphthalein as indicator, to very faint pink color. Adjust to pH 8.3, using pH meter. Add exactly 10 ml. dithizone solution (1+1) and 10 ml. carbamate solution and shake for 2 min. Allow phases to separate. Transfer CCl<sub>4</sub> (dithizone) phase to clean funnel and remove excess dithizone with 25 ml. 0.01 N NH<sub>4</sub>OH. Allow phases to separate and run enough of zinc

Procedure (Cont'd)

dithizonate through to clear water from stopcock. Dry stem and draw off zinc dithizonate into 30 ml. beaker. Pipette exactly 5 ml. into 25 ml. volumetric flask and dilute to volume with pure  $\text{CCl}_4$ . Determine color intensity with photoelectric colorimeter using green (#54) filter and setting 100% light transmission for pure  $\text{CCl}_4$  (not the blank).

Calculate amount of Zn in both blank and unknown from curve prepared as follows: Measure suitable aliquots (containing 0.002 to 0.020 mg. Zn) from standard solution into separatory funnels and proceed exactly as for unknown (see previous paragraph) from where it says " . . . . . dilute to 25 ml. volume with 0.02 N HCl . . . . " Express as p.p.m. air-dried soil.

## MINOR CONSTITUENTS (Mn, Cu, Co, Zn, Pb), TOTALS

### 7. Lead

#### Reagents

1. Hydrochloric acid - 0.02 N HCl, prepared from constant boiling HCl.
2. Ammonium citrate buffer - see under section 3. Separation of Cu, etc.
3. Dithizone reagent - see under section 3. Separation of Cu, etc.
4. Potassium cyanide - KCN, 10% solution.
5. Ammonium hydroxide - 0.01 N  $\text{NH}_4\text{OH}$ .
6. Standard lead solution. Weigh exactly 0.1598 g. dried (at 110 °C.) c. p.  $\text{Pb}(\text{NO}_3)_2$ , place in liter volumetric flask, dissolve in  $\text{HNO}_3$  (1%) and dilute to volume with the  $\text{HNO}_3$ . 1 ml. = 0.1 mg. Pb. A more convenient working standard is prepared by diluting this solution to concentration of 0.001 mg. Pb per ml.

#### Procedure

From separatory funnel containing 0.02 N HCl extract (Section 3, Procedure, para. e), take aliquot equivalent to 0.8 g. soil. Place aliquot in clean, separatory funnel and dilute to 25 ml. volume with 0.02 N HCl. Add 5 ml. ammonium citrate buffer and 10 ml. 10% KCN solution. Titrate with ammonia to maximum blue color of thymol blue indicator. Adjust to pH 9.3, using pH meter. Add exactly 10 ml. dithizone solution and shake for 3 min. Allow phases to separate. Transfer  $\text{CCl}_4$  phase to clean separatory funnel and wash out excess dithizone with 50 ml. 0.01 N  $\text{NH}_4\text{OH}$ . Clear moisture from stem of funnel with small amount of the lead dithizonate. Run lead dithizonate into colorimeter tube through pledget of cotton placed in stem of funnel. Determine color intensity with photoelectric



Procedure (Cont'd)

colorimeter, using green (#54) filter and setting 100% light transmission for pure  $\text{CCl}_4$  (not the blank) .

Calculate amount of Pb in both blank and unknown from curve prepared as follows: Measure suitable aliquots (containing 0.002 and 0.020 mg. Pb) from standard solution into separatory funnels and proceed exactly as for unknown (see previous paragraph) from where it says: " . . . . . dilute to 25 ml. volume with 0.02 N HCl . . . . . " Express as p.p.m. air-dried soil .

## MOLYBDENUM, TOTAL

### Reagents

1. Perchloric acid -  $\text{HClO}_4$ , approx. 72% .
2. Nitric acid -  $\text{HNO}_3$ , conc., distilled .
3. Sulphuric acid -  $\text{H}_2\text{SO}_4$ , conc .
4. Hydrochloric acid -  $\text{HCl}$ , constant boiling, redistilled (6.2 N).
5. Citric acid solution - 40% in 6 N  $\text{HCl}$  .
6. Potassium thiocyanate -  $\text{KSCN}$ , 10% solution .
7. Ferrous ammonium sulphate solution - 35 g.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 250 ml. (1 ml. = 20 mg. Fe ) .
8. Stannous chloride solution - 40%  $\text{SnCl}_2$  in dil.  $\text{HCl}$  (16 ml. 6.2 N  $\text{HCl}$  to 100 ml. ) .
9. Ethyl ether - Reagent grade .
10. Iso-amyl alcohol .
11. Standard molybdenum solution - Dissolve 0.15 g.  $\text{MoO}_3$  in 10 ml. 0.1 N  $\text{NaOH}$ . Make slightly acid with  $\text{HCl}$  and dilute to 1 liter. 1 ml. = 0.1 mg. Mo. A more convenient working standard is prepared by diluting this solution to concentration of 0.001 mg. Mo per ml.

### Procedure

Digest 5.0 g. finely ground soil (200- to 250-mesh) with 15 ml.  $\text{HClO}_4$ , 10 ml. conc.  $\text{HNO}_3$  and 5 ml. conc.  $\text{H}_2\text{SO}_4$ , for 2 hr. in wide-mouth erlenmeyer flask covered with sealed-end funnel to reflux acid during digestion. Raise funnel after 2 hr. and evaporate solution almost to dryness. Take up in 15 ml. 6.2 N  $\text{HCl}$  and 15 ml. water and digest

Procedure (Cont'd)

on hot water bath. Bring to boil and filter into 250 ml. beaker through buchner funnel, using filter aid to assist filtering. Wash well with water acidified with HCl. Evaporate to dryness, finally driving off last of  $\text{H}_2\text{SO}_4$  in muffle furnace at  $320^\circ\text{C}$ . Cool.

Add 40 ml. 6.2 N HCl, boil and digest until salts are dissolved. (In clay soils, some sulphates usually remain insoluble.) Evaporate to about 10 to 15 ml.

Transfer to 125 ml. separatory funnel with hot 6.2 N HCl to about 25 ml. volume. Add 4 ml. 40% citric acid. Cool. Remove Fe and Mo with four ether extractions of 25 ml. each. Shake combined ether extractions with three 10 ml. portions of water. Run combined water extractions into 100 ml. beaker and evaporate to about 5 ml.

Add exactly 4 ml. 6.2 N HCl and transfer to 125 ml. separatory funnel with water. Add 1 ml.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution (as for the blank - see below). Add 3 ml. KSCN solution, then sufficient (4 ml.)  $\text{SnCl}_2$  solution to destroy red color. Dilute to exactly 25 ml. Add 10 ml. iso-amyl alcohol and shake vigorously for 40 sec. Allow phases to separate. (Stannic oxide produced has stabilizing action when solution is shaken and water-in-alcohol emulsion may be produced.) Draw off alcohol phase into centrifuge tube, centrifuge for 10 min., then gently transfer to colorimeter tube. Keep tube stoppered. (At this point, a faint red color may develop due to oxidation in transferring solution but it will gradually fade.) Determine color intensity in photoelectric colorimeter, using blue (#42) filter.

### Procedure (Cont'd)

(If, during reading time, solution becomes cloudy, this appears to be due to  $\text{SnCl}_2$  dissolved in alcohol coming out on cooling. If tube is warmed a little, solution will clear.) .

Calculate amount of Mo from curve prepared as follows: Measure suitable aliquots (containing 0.001 to 0.01 mg. Mo) from standard solution into 125 ml. separatory funnels each containing 4 ml. 6.2 N HCl. Add 6 ml.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution to approximate amount of Fe found in soil. Proceed as in previous paragraph from where it says "Add 3 ml. KSCN solution . . . . ." Express as p.p.m. air-dried soil.

N.B. With each series of soils being analyzed, run blank to which is added 1 ml.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution.

### References

1. Chemical methods for minor elements in plants and soil. A.L. Prince, Ed. N. J. Agr. Expt. Sta., New Brunswick, N.J. 1952.
2. Kidson, E.B. Molybdenum content of Nelson soils. New Zealand J. Sci. Technol. 36A: 8-45. 1954.
3. Perrin, D.D. Determination of molybdenum in soils. New Zealand J. Sci. Technol. 28A: 183-187. 1946.
4. Sandell, E.B. Colorimetric determination of traces of metals. Vol. 3. Interscience Publishers Inc., New York. 1950.

## MANGANESE, EXCHANGEABLE and EASILY REDUCIBLE

### Reagents

1. Ammonium acetate - Neutral 1.0 N  $\text{NH}_4\text{OAc}$ . Dissolve 1540 g. ammonium acetate ( $\text{NH}_4\text{OAc}$ ) in water. Filter and dilute to 20 l. Mix thoroughly. Adjust to pH 7.0 with  $\text{NH}_4\text{OH}$  or  $\text{HOAc}$  as required.
2. Ammonium acetate - Neutral 1.0 N  $\text{NH}_4\text{OAc}$ , as above, containing 0.2% hydroquinone.
3. Nitric acid -  $\text{HNO}_3$ , conc.
4. Hydrochloric acid -  $\text{HCl}$ , conc.
5. Aqua regia - Mix 3 parts conc.  $\text{HCl}$  and 1 part conc.  $\text{HNO}_3$ .
6. Phosphoric acid solution - 4.5 ml. 85%  $\text{H}_3\text{PO}_4$  in 50 ml. water.
7. Potassium periodate -  $\text{KIO}_4$ .
8. Distilled water - boiled and containing 5 drops  $\text{H}_3\text{PO}_4$  (85%) and few grains  $\text{KIO}_4$  per liter.
9. Standard manganese solution - Dissolve 0.2876 g. freshly ground and dried  $\text{KMnO}_4$  in 20 ml. water. Reduce  $\text{KMnO}_4$  with 0.1 N oxalic acid in presence of sufficient  $\text{H}_2\text{SO}_4$ . Dilute to 1 liter. Mix thoroughly.  
1 ml. = 0.1 mg. Mn.

### Procedure

#### a. Exchangeable manganese

Place 25 g. 2 mm. soil in 500 ml. erlenmeyer flask, add 250 ml. neut. 1.0 N  $\text{NH}_4\text{OAc}$  solution and shake for 30 min. on shaker. Let stand for 6 hr. with occasional shaking. Filter. (Return soil and filter paper to flask for determination of easily reducible Mn.) Evaporate 200 ml. of filtrate to thick syrup in 250 ml. beaker, add 10 ml. aqua regia and, when



Procedure (Cont'd)

action ceases, evaporate to dryness on hot plate. Add 5 ml. conc.  $\text{HNO}_3$ , again evaporate to dryness and continue heating for at least 15 min. to remove most of acetates. Transfer to muffle furnace and ignite at  $500^\circ\text{C}$ . for 30 min. Cool. Take up residue in 10 ml. conc.  $\text{HCl}$  and boil to ensure complete solution of Mn. Evaporate to dryness.

Drive off all chlorides by three successive additions of 5 ml. conc.  $\text{HNO}_3$ , taking to dryness on water bath after each addition. Add 50 ml.  $\text{H}_3\text{PO}_4$  solution (containing 4.5 ml. 85%  $\text{H}_3\text{PO}_4$ ), boil to dissolve all salts, then cool. Add 0.4 g.  $\text{KIO}_4$ , boil for 3 min. on hot plate, then let stand on hot water bath for 30 min. Cool and make to 100 ml. with distilled water containing  $\text{H}_3\text{PO}_4$  and  $\text{KIO}_4$ . Determine color intensity with photoelectric colorimeter using green (#54) filter and setting 100% light transmission for a blank which has been carried through same procedure. (Any cloudiness in solution must be removed by centrifuging before being read in colorimeter.)

Calculate amount of Mn from curve prepared as follows: Measure suitable aliquots (containing 0.05 to 1.00 mg. Mn) from standard solution into 250 ml. beakers, evaporate to dryness and proceed as in previous paragraph from where it says: "Drive off all chlorides . . . . ." Express as p.p.m. air-dried soil.

b. Easily reducible manganese

To soil remaining after extraction of exchangeable Mn (Procedure a., 1st para.), add 250 ml. of the  $\text{NH}_4\text{OAc}$  solution containing 0.2% hydro-

### Procedure (Cont'd)

quinone. Shake at frequent intervals over period of 6 hr. Filter. Evaporate 100 ml. of filtrate to thick syrup in 250 ml. beaker and proceed as under determination of exchangeable Mn from where it says: ". . . . add 10 ml. of aqua regia . . . . ." Express as p.p.m. air-dried soil.

### References

1. Leeper, C.W. Manganese deficiency of cereals, plot experiments and a new hypothesis. Proc. Roy. Soc. Victoria 47 (11) N.S.: 225-261. 1935.
2. Leeper, C.W. The forms and reactions of manganese in the soil. Soil Sci. 63: 79-93. 1947.
3. Piper, C.S. Soil and plant analysis. Interscience Publishers Inc., New York. 1944.
4. Sherman, G.D., J.S. McHargue and W.S. Hodgkiss. Determination of active manganese in soil. Soil Sci. 54: 253-257. 1942.

## BORON, WATER-SOLUBLE

Reagents (N. B. All reagents should be tested to make sure they are boron-free)

1. Ethyl alcohol - 95%  $C_2H_5OH$ .
2. Turmeric solution - Place 0.4 g. turmeric powder in 40 ml. 95%  $C_2H_5OH$ . Shake. Make fresh daily and prepare night before use.
3. Hydrochloric acid-oxalic acid solution - Dissolve 4 g.  $H_2C_2O_4$  in 20 ml. water and add 5 ml. conc.  $HCl$ . Use warm in order to keep oxalic acid in solution.
4. Calcium hydroxide suspension. Shake 0.4 g.  $Ca(OH)_2$  (ground to pass 100-mesh) in 100 ml. water.
5. Standard boron solution. Dissolve 57.16 mg. boric acid (equivalent to 10 mg. boron) in water in 200 ml. volumetric flask. Mix thoroughly. 1 ml. = 0.05 mg. B. Dilute aliquot to obtain solution in which 1 ml. = 0.0005 mg. B.

### Procedure

Place 10 g. air-dried 2 mm. soil in 250 ml. boron-free glass erlenmeyer flask and add 50 ml. water. Connect flask with reflux condenser of boron-free glass, boil for 5 min., remove, cover with watch-glass and allow to cool at room temperature for 2 hr. When cool, shake flask and allow soil to settle.

Decant supernatant liquid into centrifuge tube of boron-free glass and centrifuge for 1 hr. or until clear solution is obtained. Pipette 10 ml. of clear solution (equivalent to 2 g. soil) into 100 ml. silica dish with 5 ml.

### Procedure (Cont'd)

$\text{Ca}(\text{OH})_2$  suspension and evaporate to dryness on water bath. Ignite in muffle furnace at  $650^\circ\text{C}$ . for 5 min. to remove organic matter and nitrates.

Add 1 ml.  $\text{HCl}$ -oxalic acid solution to residue in silica dish, wet all residue, add 2 ml. turmeric solution and mix well by rotating dish.

Take to dryness and bake on water bath kept at constant vapor temperature of from  $53^\circ$  to  $55^\circ\text{C}$ . for 2 hr. without further mixing. At end of that time, remove dish, cool, add alcohol to extract colour, and filter into 50 ml. volumetric flask. Wash all colour from dish and filter paper with alcohol and dilute to volume. Mix thoroughly.

Determine color intensity with photoelectric colorimeter, using green (#54) filter and setting 100% light transmission for a blank which has been carried through same procedure.

Calculate amount of B from curve prepared as follows: Measure suitable aliquots (containing 0.0005 to 0.0040 mg. B) from standard solution into 100 ml. silica dishes, add 5 ml.  $\text{Ca}(\text{OH})_2$  suspension to each and proceed as in method from where it says: "... evaporate to dryness on water bath". Express as p.p.m. air-dried soil.

### Precautions

- (1) All analyses must be carried out following the same procedure as to temperature, time, etc. as that used in the preparation of the standard curves.



### Precautions (Cont'd)

- (2) The blank should be constant each day.
- (3) Filter papers must be well washed with hot HCl (1+1), hot water and alcohol.
- (4) All dishes, flasks and funnels must be washed with hot water immediately before using.

### References

1. Naftel, J.A. Colorimetric microdetermination of boron.  
Ind. Eng. Chem., Anal. Ed. 2: 407-409. 1939.
2. Haas, A.R.C. The turmeric determination of water-soluble boron in soils of citrus orchards in California. Soil Sci. 58: 123-137. 1944.







